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EPA METHOD STUDY 12

CYANIDE IN WATER

by

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EPA Method Study 12, Cyanide in Water reports the results of a study by EMSL-Cincinnati for the parameters, Total Cyanide and Cyanides Amendable to Chlorination, present in water at microgram per liter levels. Four methods: pyridine-pyrazolone, pyridine-barbituric acid, electrode and Roberts-Jackson were used by 112 laboratories in Federal and State agencies, municipalities, universities, and the private/industrial sector.

Sample concentrates were prepared in pairs with similar concentrations at each of three levels. Analysts diluted samples to volume with distilled and natural waters and analyzed them. Precision, accuracy, bias and the natural water interference were evaluated for each analytical method and comparisons were made between the four methods.

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FOREWORD

Environmental measurements are required to determine the quality of drinking waters, ambient waters and the character of wastes and effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments and solid wastes.
- Investigate methods for the concentration, recovery and identification of viruses, bacteria and other microorganisms in water.
- Determine the responses of aquatic organisms to water quality.
- Develop an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication of the Environmental Monitoring and Support Laboratory, Cincinnati, entitled EPA Method Study 12, Cyanides in Water reports the results of an EPA study of analyses for Total Cyanide and Cyanide Amenable to Chlorination when present in water at microgram per liter levels. Four methods of analysis: pyridine-pyrazolone, pyridine-barbituric acid, electrode and Roberts-Jackson were used. Federal agencies, States, municipalities, universities, private laboratories and industry should find this evaluative study of the selected methods of analysis for cyanides to be helpful in their efforts to monitor and control pollution in the environment.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

PREFACE

The Environmental Monitoring and Support Laboratory (EMSL), Cincinnati, of the Office of Research and Development, is responsible for insuring the reliability of physical, chemical, biological and microbiological data generated in the water program of the EPA.

Within EMSL, the Quality Assurance Branch (QAB) conducts interlaboratory studies for method validation, laboratory evaluation and certification. It also provides check samples and develops quality control guidelines for water laboratories.

This report describes one study in the method validation series conducted by the Quality Assurance Branch.

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ABSTRACT

EPA Method Study 12, Cyanide in Water reports the results of a study by EMSL-Cincinnati for the parameters, Total Cyanide and Cyanides Amenable to Chlorination, present in water at microgram per liter levels. Four methods pyridine-pyrazolone, pyridine-barbituric acid, electrode and Roberts-Jackson were used by 60 laboratories in Federal and State agencies, municipalities, universities, and the private/industrial sector.

Sample concentrates were prepared in pairs with similar concentrations at each of three levels. Analysts diluted the samples to volume with distilled and natural waters for analysis. Precision, accuracy, bias and the natural water interference were evaluated for each analytical method and comparisons were made between the four methods.

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EPA-287 (Cin.)
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CONTENTS

	Page
FOREWORD	iii
PREFACE	iv
ABSTRACT	v
FIGURES	viii
TABLES	ix
ACKNOWLEDGMENTS	xii
PARTICIPATING LABORATORIES	
EPA Laboratories	xiii
Non-EPA Laboratories	xiv
INTRODUCTION	1
Cyanide Parameters	1
Analytical Methods for Cyanides	2
CONCLUSIONS	3
DESCRIPTION OF STUDY	
Design of Study	4
Preparation of Samples	4
Conduct of the Study	5
TREATMENT OF DATA	
Presentation of Results	6
Raw Data	6
Rejection of Outliers	6
Rejection of "Less Than" Values	7
Data Summaries	7
Statistical Summaries	7
Single Analyst Precision	8
Statements of Method Precision	8
Statements of Method Accuracy	8
Two Sample (Youden) Plots	8

CONTENTS
(continued)

DISCUSSION

	Page
Total Cyanide, General Observations	10
Total Cyanide, Pyridine-Barbituric Acid Method	11
Total Cyanide, Pyridine-Pyrazolone Method	21
Total Cyanide, Electrode Method	31
Summary for Total Cyanide in Natural Water	41
Cyanide Amenable to Chlorination, General Observations	41
CATC, Pyridine-Barbituric Acid Method	42
CATC, Pyridine-Pyrazolone Method	52
CATC, Electrode Method	62
Summary for CATC in Natural Water	72
Roberts-Jackson Method	73
REFERENCES	82
APPENDICES	
A. Instructions for EPA Method Study 12, Cyanide	83
B. Required Methods for EPA Method Study 12, Cyanide	88
Cyanide, Total (Pyridine-Barbituric Acid Method)	89
Cyanide, Total (Pyridine-Pyrazolone Method)	89
Cyanide, Total (Electrode Procedure)	98
Cyanide, Amenable to Chlorination	100
Roberts-Jackson Method	102

FIGURES

Number		Page
1	Regression Results for Total Cyanide, Pyridine-Barbituric Acid Method	18
2	Youden Plots for Total Cyanide, Pyridine-Barbituric Acid Method.	19
3	Regression Results for Total Cyanide, Pyridine-Pyrazolone Method	28
4	Youden Plots for Total Cyanide, Pyridine-Pyrazolone Method	29
5	Regression Results for Total Cyanide, Electrode Method	38
6	Youden Plots for Total Cyanide, Electrode Method	39
7	Regression Results for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method	49
8	Youden Plots for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method	50
9	Regression Results for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method	59
10	Youden Plots for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method	60
11	Regression Results for Cyanide Amenable to Chlorination, Electrode Method	69
12	Youden Plots for Cyanide Amenable to Chlorination, Electrode Method	70
13	Regression Results for Cyanide by the Roberts-Jackson Method	79
14	Youden Plots for Cyanide by the Roberts-Jackson Method	80

TABLES

Number		Page
1	Raw Data for Total Cyanide, Pyridine-Barbituric Acid Method, Recovery of Increment from Distilled Water.....	12
2	Raw Data for Total Cyanide, Pyridine-Barbituric Acid Method, Recovery of Increment from Natural or Effluent Water.....	13
3	Data Summaries for Total Cyanide, Pyridine-Barbituric Acid Method (Low Concentration Pair).....	14
4	Data Summaries for Total Cyanide, Pyridine-Barbituric Acid Method (Medium Concentration Pair).....	15
5	Data Summaries for Total Cyanide, Pyridine-Barbituric Acid Method (High Concentration Pair).....	16
6	Statistical Summary, Total Cyanide by Pyridine-Barbituric Acid Method.....	17
7	Raw Data for Total Cyanide, Pyridine-Pyrazolone Method, Recovery of Increment from Distilled Water.....	22
8	Raw Data for Total Cyanide, Pyridine-Pyrazolone Method, Recovery of Increment from Natural or Effluent Water.....	23
9	Data Summaries for Total Cyanide, Pyridine-Pyrazolone Method, (Low Concentration Pair).....	24
10	Data Summaries for Total Cyanide, Pyridine-Pyrazolone Method, (Medium Concentration Pair).....	25
11	Data Summaries for Total Cyanide, Pyridine-Pyrazolone Method, (High Concentration Pair).....	26
12	Statistical Summary, Total Cyanide by Pyridine-Pyrazolone Method	27
13	Raw Data for Total Cyanide, Electrode Method, Recovery of Increment from Distilled Water.....	32
14	Raw Data for Total Cyanide, Electrode Method, Recovery of Increment from Natural or Effluent Water.....	33

TABLES
(continued)

Number		Page
15	Data Summaries for Total Cyanide, Electrode Method (Low Concentration Pair).....	34
16	Data Summaries for Total Cyanide, Electrode Method (Medium Concentration Pair).....	35
17	Data Summaries for Total Cyanide, Electrode Method (High Concentration Pair).....	36
18	Statistical Summary, Total Cyanide by Electrode Method.....	37
19	Raw Data for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method, Recovery of Increment from Distilled Water.	43
20	Raw Data for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method, Recovery of Increment from Natural or Effluent Water.....	44
21	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method (Low Concentration Pair).....	45
22	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method (Medium Concentration Pair).....	46
23	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method (High Concentration Pair).....	47
24	Statistical Summary, Cyanide Amenable to Chlorination by Pyridine-Barbituric Acid Method.....	48
25	Raw Data for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method, Recovery of Increment from Distilled Water.....	53
26	Raw Data for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method, Recovery of Increment from Natural or Effluent Water.....	54
27	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method (Low Concentration Pair).....	55
28	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method (Medium Concentration Pair).....	56
29	Data Summaries for Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method (High Concentration Pair).....	57

TABLES
(continued)

Number		Page
30	Statistical Summary, Cyanide Amenable to Chlorination by Pyridine-Pyrazolone Method.....	58
31	Raw Data for Cyanide Amenable to Chlorination, Electrode Method, Recovery of Increment from Distilled Water.....	63
32	Raw Data for Cyanide Amenable to Chlorination, Electrode Method, Recovery of Increment from Natural or Effluent Water.....	64
33	Data Summaries for Cyanide Amenable to Chlorination, Electrode Method (Low Concentration Pair).....	65
34	Data Summaries for Cyanide Amenable to Chlorination, Electrode Method (Medium Concentration Pair).....	66
35	Data Summaries for Cyanide Amenable to Chlorination, Electrode Method (High Concentration Pair).....	67
36	Statistical Summary, Cyanide Amenable to Chlorination by Electrode Method.....	68
37	Raw Data for Cyanide by the Roberts-Jackson Method, Recovery of Increment from Distilled Water.....	74
38	Raw Data for Cyanide by the Roberts-Jackson Method, Recovery of Increment from Natural or Effluent Water.....	74
39	Data Summaries for Cyanide by the Roberts-Jackson Method (Low Concentration Pair).....	75
40	Data Summaries for Cyanide by the Roberts-Jackson Method (Medium Concentration Pair).....	76
41	Data Summaries for Cyanide by the Roberts-Jackson Method (High Concentration Pair).....	77
42	Statistical Summary, Cyanide by the Roberts-Jackson Method.....	78

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INTRODUCTION

Cyanides are common constituents in a variety of industrial wastes such as quench waters from coke plants and blast furnaces, and the rinse waters from heat treating and metal finishing operations. In addition to these metal industries, other industrial operations, particularly chemical manufacturing, utilize and discharge cyanide compounds. Because of the extreme toxicity of the cyanide ion to aquatic life and to humans, rigorous treatment of wastewaters containing cyanide is required.

The measurement of cyanides in the analytical laboratory is complicated by the ease with which the cyanide ion complexes with other metal ions. Complexing occurs in several ways with metals. For example, cyanide combines with iron to form ferrous cyanide, $Fe(CN)_2$; ferric cyanide, $Fe(CN)_3$; ferrous ferricyanide $Fe_3\{Fe(CN)_6\}_2$; ferric ferricyanide $Fe\{Fe(CN)_6\}$; ferrous ferrocyanide, $Fe_2\{Fe(CN)_6\}$ and ferriferrocyanide, $Fe\{Fe(CN)_6\}_3$. Similarly, copper may form a series of copper-iron-cyanide complexes. Other metals such as cadmium, silver, tin, zinc and lead form simple cyanides ($Cd(CN)_2$, $Ag(CN)_2$, and so on, as well as the metal-iron-cyanide complexes.

At the normal pH's and temperatures of streams, the dissociated cyanide ion (CN^-) is toxic to most species of fish at a level of 0.1 mg/liter. Complexed cyanides are far less toxic and discharge of relatively large concentrations of these compounds to receiving streams is not immediately harmful. Consequently, it has been suggested that cyanide be complexed with metals such as iron, prior to discharge, to reduce toxicity. However, enforcement authorities are reluctant to authorize cyanide discharge, even complex cyanides, because such complexes may revert to simpler, more toxic forms under the influence of stream pH, temperature, and ultra-violet radiation.

Cyanide Measurements

Cyanide is usually measured as the following parameters: free cyanide, cyanide amenable to chlorination and total cyanide[1, 2].

Free or simple cyanide such as NaCN, KCN or HCN is directly measureable by volumetric titration or colorimetry.

Cyanide Amenable to Chlorination measures common metal cyanide compounds and most complexes except for the iron cyanides. The sample is divided into two parts and total cyanide is determined before and after an alkaline chlorination step. Cyanides amenable to chlorination are the difference between the two total cyanide analyses. The method is equivalent to ASTM, Annual Book of ASTM Standards; 11.02, Water, D2036-82, Method B-Cyanide Amenable to Chlorination by Difference, p. 113, 1983.

Total Cyanide is a measure of all cyanides including iron cyanide complexes after conversion to HCN by acidification, distillation and absorption in an NaOH scrubber. The cyanide is titrated as HCN against a silver nitrate solution or is converted to cyanogen chloride and read colorimetrically using a pyridine-pyrazolone or pyridine-barbituric acid reagent.

Analytical Methods for Cyanide

The methods for the measurement of cyanide have been a subject of debate and dissatisfaction among environmental chemists for many years. Unfortunately, the complexing properties of the cyanide radical which make it useful in metal plating operations are the same properties which make definition and measurement difficult. Current analytical methods can directly measure cyanide-metal complexes and cannot uniformly breakdown the complexes for measurement as simple cyanide.

The analytical methods attempt to isolate the cyanide as sodium cyanide, using a distillation or stripping action, with absorption of gaseous hydrogen cyanide (HCN) as a basic solution followed by a colorimetric measurement. The methods of distillation stripping and the color forming reagents used vary. Cyanide ions may also be measured electrometrically using an ion selective electrode, but despite its speed and simplicity the method has not been widely accepted. So called free cyanide, such as sodium or potassium cyanide, is also frequently determined volumetrically by titration with silver nitrate, but the procedure is not useful for the below one (1) microgram levels of cyanide found in many wastewaters. Cyanide amenable to chlorination also employs the usual colorimetric methods, but measures total cyanide before and after oxidation of the sample by chlorination with Chloramine-T.

With the variety of methods available and the (lack of concensus) among analysts regarding the most reliable method, it was agreed that a collaborative study was required to ascertain, if possible, which method should be adopted for general use. The following methods were subsequently chosen for collaborative testing:

1) Serfass distillation/pyridine-barbituric acid colorimetric method.

2) Serfass distillation/pyridine-pyrazolone colorimetric method.

3) Serfass distillation/ion-selective electrode.

Participants were requested to analyze for both total cyanide and cyanide amenable to chlorination, using Serfass distillation and their choice of detection method listed above. However, participants were encouraged to use the barbituric acid method if possible.

Upon receiving the invitation to participate in the study, a number of industrial labs indicated they would also like to provide data using the Roberts-Jackson method of measuring simple cyanides. This method uses the conventional colorimetric procedures, but modifies the distillation so that only simple cyanides are measured.

CONCLUSIONS

Total Cyanide

For the total cyanide parameter, statistics for the pyridine-barbituric acid and pyridine-pyrazolone methods were very similar. The electrode method showed significantly greater data variability. However, all three methods seem capable of producing valid data in the hands of a skilled analyst.

Cyanide Amenable to Chlorination

Although the pyridine-barbituric acid method showed the least bias and the smallest standard deviation, none of the three methods tested provided satisfactory data for the CATC parameter. As a corollary, CATC did not provide a reliable means for distinguishing between free and complexed cyanides.

Roberts-Jackson

The generation of data by the Roberts-Jackson method was encouraged, but only three labs submitted results and one of these sets was incomplete.

On the basis of the limited data obtained in this study, the Roberts-Jackson method shows promise of improved accuracy and precision, while providing greater safety by avoiding the open generation of toxic cyanogen chloride. However, because of limited data this study did not establish its real value.

General Conclusion

The compelling reason for preferring the pyridine-barbituric acid method over the pyridine-pyrazolone method is convenience rather than statistical improvement in the data produced.

DESCRIPTION OF STUDY

Design of Study

The study design is based on Youden's non-replicate technique for the collaborative study of analytical methods. Using this design, sample pairs were developed with slightly different concentrations of the constituents, at each of several levels. The analyst is directed to do a single analysis and report one value for each sample, as in normal routine.

In this study, six samples were prepared as concentrates in sealed glass ampuls and presented to the analyst as unknowns. Three levels of cyanide concentration in three pairs of samples were tested at levels typical of those observed in wastewaters.

The analyst was directed to dilute a 5.0 mL aliquot of each concentrate to one liter volume with distilled water and a second 5.0 mL aliquot to one liter volume with a natural or effluent water. Natural or effluent water samples were analyzed with and without incremental aliquots and the recovery determined by difference. Each sample was analyzed only once. Analysis in distilled water evaluated the proficiency of the analyst in using the method on a sample free of interferences, while recovery of the increment from a natural or effluent water, such as river, lake, or an estuary, indicated whether the method was affected by interferences in these waters.

Data were recorded on standard forms and returned to EMSL-Cincinnati for statistical evaluation and preparation of the report.

Preparation of Samples

Sample concentrates were prepared by dissolving precisely weighed amounts of reagent grade chemicals in high purity water obtained by passing distilled water through a four cartridge Millipore Super-Q System, to produce accurate levels of simple and complex cyanides. Each sample contained simple and complex cyanides, present as potassium cyanide and potassium ferrocyanide, respectively. The concentrates were preserved with sodium hydroxide and checked by repeated analyses over a period of three months to confirm the calculated concentrations and the stability of the samples. Analyses of the samples by an outside laboratory confirmed the data of the Quality Assurance Branch, EMSL-Cincinnati.

When diluted to volume according to the instructions, the samples contained concentrations of cyanide as shown:

True Values for Cyanide Concentrations*

Sample	Total Cyanide µg/L	Cyanide Amenable to Chlorination, µg/L
1	25	13
2	372	149
3	35	18
4	106	64
5	106	64
6	352	141

*The concentrations were the actual levels calculated and added. Analyses were used for verification only.

Conduct of the Study

An invitational memorandum announced the study to the ten EPA Regions and to the ASTM D-19 committee members in October, 1974. A separate invitational letter was sent to industrial laboratories known to be routinely analyzing wastes for cyanides. Although it was estimated to require a minimum of one workweek of analytical effort, 112 laboratories from EPA, other Federal, State and local agencies, Canadian groups, universities and private industry agreed to participate.

Each participant received a set of six ampuls, instructions for sample preparation, duplicate report sheets (Appendix A), and a copy of the analytical procedures to be used. The participating laboratories were required to analyze samples using methods from EPA's Methods of Chemical Analysis of Water and Wastes, 1974, EMSL-Cincinnati. However, a number of industrial laboratories participating in this study asked if it would be agreeable with EPA if they performed the cyanide analyses by a modified Roberts-Jackson method as well as by the pyridine methods. EPA agreed. Appendix B provides description of EPA methodologies, the original Roberts-Jackson paper, and the Woods River modification (Shell Oil Company) which the industrial laboratories used in this study. Participants were allowed fifty days to complete the analyses and report the data. Data reported later than the cut off date were omitted. Fifty-six laboratories returned data in time to be included in this report.

GENERAL TREATMENT OF DATA

Presentation of Results

For discussion purposes, the results of the cyanide study are organized into subsections by parameter and by analytical procedures within that parameter. In order of appearance, these subsections are:

Total Cyanide, Pyridine-Barbituric Acid Method
Total Cyanide, Pyridine-Pyrazolone Method
Total Cyanide, Electrode Method

Cyanide Amenable to Chlorination, Pyridine-Barbituric Acid Method
Cyanide Amenable to Chlorination, Pyridine-Pyrazolone Method
Cyanide Amenable to Chlorination, Electrode Method

Roberts-Jackson Method

Raw Data

The raw data for each analyst are presented in the first two tables of each subsection and are identified by laboratory code number.

Rejection of Outliers

Abnormal values known as outliers resulting from chemical, instrumental and analyst error, are a part of the raw data generated in every collaborative study. Since true outliers reflect unusual random or systematic error, they should be eliminated so that they do not inflate unrealistically the measure of deviation of the procedure tested. In this study, outliers were rejected by one procedure for sets of twenty-five values or less ($n \leq 25$), and by another procedure for larger sets ($n > 25$). The procedure for small sets used the technique recommended in American Society for Testing and Materials, Part 31, Determination of Precision and Bias of Methods of Committee D-19 on Water, D-2777-77. Using the formula:

$$T_i = (X_i - \overline{X})/S$$

Where X_i = value being tested

$\overline{X}$ = average of all values in the series containing X_i

S = standard deviation of all value in the series containing X_i

T_i = T value for X_i

When T_i is greater than the critical value given in the T table for the 1% significance level (99% confidence level), there is a 99 to 1 assurance that X_i is indeed a true outlier and should be discarded. If X_i is found to be an outlier, the process is repeated using the remaining data until all outliers have been identified. Values found to be outliers are shown as rejected values in the raw data tables.

For data sets of more than twenty-five values ($n > 25$), outliers were rejected by applying a two stage procedure. In the first stage, the initial mean ($\bar{X}$) and standard deviation (S) of the data set were calculated and any values beyond $\bar{X} \pm 4\ S$ were identified as outliers. At stage two, the mean ($\bar{X}'$) and standard (S') were calculated from the remaining n' values. Any values beyond $\bar{X}' \pm t_{.99}(n'-1)S'$, where $t_{.99}(n'-1)$ is the Student's t value for n'-1 degrees of freedom and a 99 percent confidence level, were also identified as outliers. As with the other procedure, outliers are shown as rejected values in the raw data tables.

Rejection of "Less Than" Values

Approximately one third of all background levels for the natural water analyses were reported as "less than" values. Apparently a number of analysts did not detect cyanide in the natural water substrate, or only observed what they believed to be a trace of cyanide. In such cases, the background cyanide was often reported as a "less than" value, for example <20 µg/L. If the spike plus background value was then reported as 230, the recovery could only be calculated as 230 - <20 = <230. Such "less than" values were not statistically usable and are also shown as rejected values in the tables of reported data.

Data Summaries

Data summaries are given in the next three tables of each discussion subsection. Each table provides a statistical evaluation of the data for a pair of concentrates in distilled and natural waters. In addition to the statistical measurements retained, data are ranked in ascending order and graphically presented in a histogram using $\sqrt{n}$ cell divisions. Each X in the histogram represents a single analytical result for up to 15 values/cell. When more than 15 values/cell occur, only 15 X's are printed but the true number of values included in the cell is shown at the left.

Significant Digits for Data

In the raw data and data summary tables, all data were reported to two decimal places for consistency, not as an indication of the proper number of significant digits.

Statistical Summaries

A statistical summary is provided as the last table of each discussion subsection. Most of these statistics have been selected from the previous data summary tables to allow a convenient comparison of the effects that concentration level and background water had on the data generated by the method under discussion.

Single Analyst Precision

In each statistical summary, the standard deviation (S) indicates the dispersion expected among values generated for a group of laboratories. This represents the broad error in any mass of data collected in a collaborative study. However, the measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single analyst precision is measured here as the S_r value. It was defined by Youden[3] as:

$$S_r^2 = \frac{\sum_{i=1}^{n} (D_i - \bar{D})^2}{2(n - 1)}$$

where: n = the number of paired observations

D_i = the difference between observations for a sample pair

$\bar{D}$ = the average value for D_i

Statements of Method Precision

For each type of water, linear regressions were produced relating the mean recovery estimates ($\bar{X}$) to the overall S and single analyst S_r precision estimates shown in the statistical summary. Plots of these regressions follow the statistical summary for each discussion subsection. Mathematical equations for the regressions are included on the plots.

Statements of Method Accuracy

For each type of water, linear regressions were also produced relating the true concentration levels to the mean recovery estimates ($\bar{X}$) shown in the statistical summary. As before, mathematical equations for the regressions are included on the plots.

Youden Plots

The second figure for each discussion subsection consists of six plots generated according to the method of Youden from the retained data for a sample pair, i.e., two samples of a similar concentration level, in distilled or natural water. The results for each of the samples in a pair were used respectively as the x and y coordinates to plot a single point for each analyst. The plot of all points for each sample pair characterizes the performance of the method for that concentration level and type of water.

If random errors were largely responsible for the spread of results around the true values, the data on a plot would be equally distributed among the four quadrants (+ +), (- +), (- -) and (+ -). However, if systematic errors were the primary source of variation, the values would not be randomly distributed, but would be grouped along a 45° slope line in the (- -) and (+ +) quadrants. This occurs because each analyst tends to get either high or low results on both samples in a pair. If the method of analysis is inherently imprecise, there will be a general scatter of data points away from the 45° line. A significant bias or interference in the method will cause the general grouping of data to be low (- -) or high (+ +) along the 45° line. Plot points far from the general cluster suggest a procedure or instrument which is out of control.

These Tables and Figures are listed on pages viii through xi.

DISCUSSION

Total Cyanide, General Observations

The total cyanide parameter measures all simple and complexed cyanides by conversion to HCN in the Serfass distillation, absorption into NaOH solution and measurement by electrometric, titrametric or colorimetric techniques. If the cyanide levels are <1 mg/liter, the more sensitive, colorimetric measurements are made using either the pyridine-pyrazalone or pyridine-barbituric acid methods.

One would expect total cyanide results to have a negative bias from incomplete conversion to HCN, loss of HCN during distillation or inefficient absorption in the caustic solution.

The pyridine-barbituric acid method is relatively new, having been developed in the last few years. By contrast, the pyridine-pyrazolone method has been in use for more than twenty years and has been the only colorimetric cyanide method recommended in standard method texts. In this study, the collaborating laboratories were requested to use the pyridine-barbituric acid method if possible, but they were permitted to use the pyridine-pyrazolone method if the analyst was not familiar with the preferred procedure. Thirty-nine of fifty-six reporting laboratories chose the newer pyridine-barbituric acid method.

For the pyridine-pyrazolone method, a mixture of two reagents must be prepared fresh on the day the test is run. For the barbituric acid method, the color-developing solution may be held for six months after preparation and as a result, is immediately available when needed. Furthermore, the barbituric acid reagent develops color in a much shorter time than the pyrazolone reagents, in eight minutes versus fifty minutes. The advantages of ease of reagent preparation and shorter color development time may have encouraged use of the newer method by a majority of the laboratories.

The electrode method is simply a probe measure of free cyanide after treatment to convert complex cyanides to a measureable form. It therefore combines the performance characteristics of the conversion and the probe sensor.

Total Cyanide, Pyridine-Barbituric Acid Method

In Tables 1 and 2, thirty-eight laboratories reported distilled water data and thirty-six reported natural water data. Natural water data from eight laboratories were rejected because the background levels were reported as "less than" values.

Some conclusions can be drawn from studying the histograms in Tables 3, 4 and 5. First, the largest group of analysts reported values quite near the true values and as anticipated, a somewhat smaller group, did not get good recovery of the increment. However, in some of the histograms, a small third group of analysts reported unusually high recoveries. These high values, which were close enough together or numerous enough to avoid being rejected as outliers, stood out because they led to blank cells and secondary peaks in the histograms. Whatever the cause, these high recoveries seem to be characteristic of the method, particularly at low concentrations.

A comparison of the statistics in Table 6 for distilled and natural waters showed no difference in recovery. If interferences had been a problem, the standard deviations for the natural waters would have been greater than those for distilled water. The standard deviations for natural water were slightly higher for the low concentration pair, but not for the higher concentration levels. The slightly higher deviations at low levels can be explained by the fact that the natural water values were obtained by subtraction of backgrounds at about the same concentration level. Such by difference results should have larger standard deviations than a similar set of direct results.

The precision and accuracy plots in Figure 1 also show little difference between distilled and natural water data. Since the regression lines fit the points quite well, the assumption of linearity appears acceptable throughout the concentration range studied.

The Youden plots in Figure 2 support the earlier conclusion, based upon the histograms, that some outliers persisted in the retained data. These extreme results show either as isolated points near a 45° line bisecting the first and third quadrants, indicating an unusual <u>systematic</u> error, or well away from the 45° line, indicating an unusual <u>random</u> error. A good example of unusual systematic error is the point near the upper right hand corner of plot C for distilled water. The effect of unusual random error can be seen in the upper left hand corner of plot B for distilled water.

TABLE 1

Raw Data for Total Cyanide
Pyridine-Barbituric Acid Method

Recovery of Increment from Distilled Water

	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Increment In µg/L	25.00	372.00	35.00	106.00	106.00	352.00
Lab Code						
102	40.00	490.00	50.00	100.00	110.00	520.00
110	28.00	194.00	47.00	37.00	43.00	213.00
112	23.00	303.00	47.00	130.00	135.00	440.00
121	20.00	480.00	40.00	120.00	110.00	280.00
122	24.00	327.00	35.00	99.00	102.00	351.00
138	46.00	540.00	70.00	118.00	108.00	306.00
157	25.00	450.00	10.00	48.00	80.00	465.00
167	20.00	317.00	28.00	87.00	89.00	370.00
197	23.00	375.00	37.00	107.00	113.00	370.00
204	24.00	385.00	32.00	104.00	99.00	330.00
211	11.00	112.00	14.00	46.00	54.00	105.00
259	22.00	342.00	32.00	102.00	99.00	314.00
388	27.00	317.00	33.00	120.00	130.00	388.00
438	22.00	258.00	38.00	62.00	72.00	252.00
481	10.00	172.00	42.00	54.00	58.00	140.00
486	38.00	373.00	38.00	116.00	113.00	357.00
566	20.00	380.00	30.00	90.00	90.00	340.00
572	26.00	398.00	30.00	70.00	104.00	325.00
624	40.00	600.00	10.00	50.00	190.00	640.00
626	28.00	440.00	31.00	107.00	99.00	320.00
627	35.00	985.00*	90.00*	305.00*	300.00*	660.00*
629	35.00	380.00	90.00*	104.00	100.00	200.00
630	10.00	335.00	36.00	102.00	99.00	327.00
631	25.00	349.00	34.00	102.00	102.00	340.00
632	14.00	197.00	17.00	66.00	52.00	178.00
633	51.00	283.00	202.00*	290.00*	251.00*	291.00
634	30.00	420.00	60.00	135.00	110.00	410.00
635	19.00	523.00	36.00	140.00	90.00	454.00
636		334.00				
639	24.00	352.00	34.00	100.00	96.00	327.00
641	24.00	275.00	25.00		38.00	235.00
643	20.00	198.00	25.00	138.00	152.00	238.00
644	25.00	360.00	35.00	102.00	100.00	350.00
645	44.00	388.00	44.00	84.00	110.00	260.00
646	17.00	217.00	17.00	75.00	71.00	250.00
647	22.00	360.00	33.00	104.00	108.00	399.00
648	22.00	333.00	26.00	95.00	87.00	325.00
649	13.00	340.00	26.00	110.00	110.00	310.00

* = Rejected

TABLE 2

Raw Data for Total Cyanide
Pyridine-Barbituric Acid Method

Recovery of Increment from Natural or Effluent Water

Increment In µg/L	Ampul 1 25.00	Ampul 2 372.00	Ampul 3 35.00	Ampul 4 106.00	Ampul 5 106.00	Ampul 6 352.00
Lab Code						
102	10.00	490.00	40.00	90.00	90.00	480.00
110	38.00	237.00	36.00	66.00	66.00	189.00
112	<12.00*	<400.00*	<47.00*	<50.00*	<130.00*	<400.00*
121	<20.00*	<450.00*	<30.00*	<110.00*	<110.00*	<370.00*
122	17.00	310.00	23.00	94.00	94.00	261.00
138	50.00	540.00	61.00	104.00	112.00	326.00
157	30.00	450.00	10.00	48.00	80.00	500.00
167		322.00	32.00	90.00	92.00	332.00
197	30.00	375.00	45.00	115.00	110.00	370.00
204	20.00	395.00	34.00	86.00	20.00	375.00
211	11.00		15.00		56.00	
259	<22.00*	<342.00*		<99.00*	<99.00*	<314.00*
388	34.00	275.00	41.00	123.00	134.00	327.00
438	15.00	260.00	25.00	63.00	67.00	237.00
481	16.00	126.00	30.00	82.00	64.00	200.00
566	20.00	390.00	35.00	95.00	100.00	360.00
572	<27.00*	<403.00*	<26.00*	<69.00*		
626	17.00	370.00		76.00	44.00	340.00
627	55.00	984.00*	90.00	325.00*	325.00*	670.00*
629	20.00	350.00	90.00	110.00	100.00	200.00
630	19.00	385.00	24.00	96.00	95.00	346.00
631	26.00	339.00	-61.00*	91.00	103.00	324.00
632	8.00	180.00	16.00	49.00	44.00	143.00
633	50.00	258.00	280.00*	283.00*	260.00	288.00
634	<30.00*	<450.00*	<50.00*		<120.00*	<410.00*
635	36.00	543.00	51.00	116.00	18.00	488.00
636		<394.00*				
639	23.00	350.00	43.00	120.00	82.00	320.00
640	20.00	380.00	30.00	90.00	80.00	300.00
641	<23.00*	<277.00*	<30.00*	<78.00*	<80.00*	<242.00*
643	<16.00*	<185.00*	<29.00*	<86.00*	<125.00*	<205.00*
644	24.00	357.00	34.00	100.00	101.00	347.00
646	33.00	<317.00*	41.00	75.00	75.00	250.00
647	<25.00*	<363.00*	<32.00*	<111.00*	<120.00*	<394.00*
648	20.00	279.00	11.00	80.00	71.00	313.00
649	14.00	324.00	26.00	84.00	84.00	304.00

* = Rejected

TABLE 3

DATA SUMMARIES FOR TOTAL CYANIDE PYRIDINE-BARBITURIC ACID METHOD LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	37
INCREMENT	25.00
MEAN	25.59
MEDIAN	24.00
SKEWNESS	.70
RANGE	41.00
VARIANCE	96.97
STANDARD DEVIATION	9.85
95% CONF. (UPPER LIM.)	45.57
INTERVAL (LOWER LIM.)	5.62
COEF. OF VAR. (AS A %)	38.47
ACCURACY (% REL. ERR.)	2.38

MIDPOINT	FREQ.	HISTOGRAM
13.417	5	XXXXX
20.250	12	XXXXXXXXXXXX
27.083	12	XXXXXXXXXXXX
33.917	2	XX
40.750	4	XXXX
47.583	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

10.00	27.00
10.00	28.00
11.00	28.00
13.00	30.00
14.00	35.00
17.00	35.00
19.00	38.00
20.00	40.00
20.00	40.00
20.00	44.00
20.00	46.00
22.00	51.00
22.00	
22.00	
22.00	
23.00	
23.00	
24.00	
24.00	
24.00	
24.00	
25.00	
25.00	
25.00	
26.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	26
INCREMENT	25.00
MEAN	25.23
MEDIAN	20.00
SKEWNESS	.87
RANGE	47.00
VARIANCE	157.62
STANDARD DEVIATION	12.55
95% CONF. (UPPER LIM.)	51.09
INTERVAL (LOWER LIM.)	-.63
COEF. OF VAR. (AS A %)	49.76
ACCURACY (% REL. ERR.)	.92

MIDPOINT	FREQ.	HISTOGRAM
12.700	8	XXXXXXXX
22.100	9	XXXXXXXXX
31.500	5	XXXXX
40.900	1	X
50.300	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

8.00	55.00
10.00	
11.00	
14.00	
15.00	
16.00	
17.00	
17.00	
19.00	
20.00	
20.00	
20.00	
20.00	
20.00	
23.00	
24.00	
26.00	
30.00	
30.00	
33.00	
34.00	
36.00	
36.00	
50.00	
50.00	

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	34
INCREMENT	35.00
MEAN	33.59
MEDIAN	33.50
SKEWNESS	.47
RANGE	60.00
VARIANCE	161.16
STANDARD DEVIATION	12.69
95% CONF. (UPPER LIM.)	59.42
INTERVAL (LOWER LIM.)	7.76
COEF. OF VAR. (AS A %)	37.80
ACCURACY (% REL. ERR.)	-4.03

MIDPOINT	FREQ.	HISTOGRAM
15.000	5	XXXXX
25.000	5	XXXXX
35.000	15	XXXXXXXXXXXXXXX
45.000	5	XXXXX
55.000	1	X
65.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

10.00	38.00
10.00	40.00
14.00	42.00
17.00	44.00
17.00	47.00
25.00	47.00
25.00	50.00
26.00	60.00
26.00	70.00
28.00	
30.00	
30.00	
31.00	
32.00	
32.00	
33.00	
33.00	
34.00	
34.00	
35.00	
35.00	
36.00	
36.00	
37.00	
38.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	24
INCREMENT	35.00
MEAN	36.79
MEDIAN	34.00
SKEWNESS	1.24
RANGE	80.00
VARIANCE	418.95
STANDARD DEVIATION	20.47
95% CONF. (UPPER LIM.)	79.13
INTERVAL (LOWER LIM.)	-5.55
COEF. OF VAR. (AS A %)	55.63
ACCURACY (% REL. ERR.)	5.12

MIDPOINT	FREQ.	HISTOGRAM
18.000	7	XXXXXXX
34.000	11	XXXXXXXXXXX
50.000	3	XXX
66.000	1	X
82.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

10.00
11.00
15.00
16.00
21.00
24.00
25.00
26.00
30.00
30.00
32.00
34.00
34.00
35.00
36.00
40.00
41.00
41.00
43.00
45.00
51.00
61.00
90.00
90.00

TABLE 4

DATA SUMMARIES FOR TOTAL CYANIDE PYRIDINE-BARBITURIC ACID METHOD MEDIUM CONCENTRATION PAIR

A) AMPUL 4

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES REC.	34
INCREMENT	100.00
MEAN	94.82
MEDIAN	102.00
SKEWNESS	-.44
RANGE	103.00
VARIANCE	760.44
STANDARD DEVIATION	27.40
95% CONF. UPPER LIM.:	150.54
INTERVAL LOWER LIM.:	39.07
COEF. OF VAR. (AS A %)	28.90
ACCURACY (% REL. ERR.):	-10.54

MIDPOINT FREQ. HISTOGRAM

45.583	5	XXXXX
62.750	3	XXX
79.917	3	XXX
97.083	12	XXXXXXXXXXXX
114.250	7	XXXXXXX
131.417	4	XXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

37.00	110.00
45.00	115.00
45.00	115.00
50.00	120.00
54.00	120.00
62.00	130.00
65.00	135.00
70.00	138.00
75.00	140.00
84.00	
87.00	
90.00	
95.00	
99.00	
100.00	
100.00	
102.00	
102.00	
102.00	
102.00	
104.00	
104.00	
104.00	
107.00	
107.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES REC.	24
INCREMENT	100.00
MEAN	84.29
MEDIAN	90.00
SKEWNESS	-.28
RANGE	75.00
VARIANCE	410.34
STANDARD DEVIATION	20.26
95% CONF. UPPER LIM.:	131.20
INTERVAL LOWER LIM.:	47.38
COEF. OF VAR. (AS A %)	24.69
ACCURACY (% REL. ERR.):	-15.76

MIDPOINT FREQ. HISTOGRAM

55.500	2	XX
70.500	4	XXXX
85.500	8	XXXXXXXX
100.500	5	XXXXX
115.500	5	XXXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

40.00	
44.00	
63.00	
66.00	
75.00	
76.00	
80.00	
82.00	
84.00	
86.00	
90.00	
90.00	
90.00	
91.00	
94.00	
95.00	
98.00	
110.00	
114.00	
115.00	
115.00	
120.00	
123.00	

B) AMPUL 5

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES REC.	35
INCREMENT	100.00
MEAN	97.00
MEDIAN	100.00
SKEWNESS	.42
RANGE	152.00
VARIANCE	859.65
STANDARD DEVIATION	29.49
95% CONF. UPPER LIM.:	157.73
INTERVAL LOWER LIM.:	37.87
COEF. OF VAR. (AS A %)	30.15
ACCURACY (% REL. ERR.):	-7.74

MIDPOINT FREQ. HISTOGRAM

50.667	5	XXXXX
76.00	6	XXXX
101.333	22	XXXXXXXXXXXXXXX
126.667	2	XX
152.00	1	X
177.333	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

38.00	115.00
43.00	110.00
52.00	110.00
54.00	110.00
58.00	115.00
71.00	115.00
76.00	130.00
80.00	135.00
87.00	152.00
89.00	190.00
90.00	
90.00	
95.00	
99.00	
99.00	
99.00	
99.00	
100.00	
100.00	
102.00	
102.00	
104.00	
108.00	
108.00	
110.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES REC.	28
INCREMENT	100.00
MEAN	86.25
MEDIAN	85.00
SKEWNESS	1.47
RANGE	242.00
VARIANCE	2080.98
STANDARD DEVIATION	44.73
95% CONF. UPPER LIM.:	174.06
INTERVAL LOWER LIM.:	-1.90
COEF. OF VAR. (AS A %)	51.88
ACCURACY (% REL. ERR.):	-13.85

MIDPOINT FREQ. HISTOGRAM

92.250	7	XXXXXXX
140.000	17	XXXXXXXXXXXXXXXXX
187.750	1	X
235.500	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

38.00	250.00
48.00	
64.00	
66.00	
68.00	
68.00	
71.00	
73.00	
75.00	
80.00	
80.00	
82.00	
84.00	
90.00	
90.00	
90.00	
90.00	
100.00	
100.00	
101.00	
105.00	
110.00	
112.00	
114.00	

TABLE 5

DATA SUMMARIES FOR TOTAL CYANIDE PYRIDINE-BARBITURIC ACID METHOD HIGH CONCENTRATION PAIR

A) AMPUL 2

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES MET.	37
INCREMENT	372.00
MEAN	348.57
MEDIAN	347.00
SKEWNESS	.06
RANGE	488.00
VARIANCE	11439.31
STANDARD DEVIATION	106.96
95% CONF. (UPPER LIM.)	391.65
INTERVAL (LOWER LIM.)	135.49
COEF. OF VAR. (AS A %)	30.14
ACCURACY (% REL. ERR.)	-4.10

MIDPOINT FREQ. HISTOGRAM

152.667	2	XX
216.00	5	XXXXX
315.333	13	XXXXXXXXXXXXX
346.667	10	XXXXXXXXXX
478.00	4	XXXX
542.333	1	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

152.00	345.00
170.00	345.00
194.00	346.00
197.00	355.00
198.00	370.00
217.00	440.00
259.00	455.00
275.00	480.00
283.00	494.00
304.00	527.00
317.00	541.00
317.00	580.00
327.00	
334.00	
334.00	
335.00	
340.00	
342.00	
344.00	
342.00	
344.00	
344.00	
345.00	
345.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES MET.	24
INCREMENT	372.00
MEAN	345.21
MEDIAN	350.50
SKEWNESS	-.06
RANGE	417.00
VARIANCE	11084.25
STANDARD DEVIATION	105.28
95% CONF. (UPPER LIM.)	390.74
INTERVAL (LOWER LIM.)	299.67
COEF. OF VAR. (AS A %)	30.50
ACCURACY (% REL. ERR.)	-4.78

MIDPOINT FREQ. HISTOGRAM

167.700	2	XX
261.100	5	XXXXX
354.500	9	XXXXXXXXX
447.900	5	XXXXX
541.300	1	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

170.00	345.00
194.00	346.00
197.00	355.00
198.00	370.00
217.00	440.00
259.00	455.00
275.00	480.00
283.00	494.00
304.00	527.00
317.00	541.00
317.00	580.00
327.00	
334.00	
334.00	
335.00	
340.00	
342.00	
344.00	
342.00	
344.00	
344.00	
345.00	
345.00	

B) AMPUL 6

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES MET.	35
INCREMENT	352.00
MEAN	325.56
MEDIAN	326.00
SKEWNESS	.44
RANGE	535.00
VARIANCE	10782.77
STANDARD DEVIATION	103.84
95% CONF. (UPPER LIM.)	536.36
INTERVAL (LOWER LIM.)	114.75
COEF. OF VAR. (AS A %)	31.90
ACCURACY (% REL. ERR.)	-7.51

MIDPOINT FREQ. HISTOGRAM

144.583	3	XXX
238.750	8	XXXXXXXX
327.917	17	XXXXXXXXXXXXXX
417.083	5	XXXXX
506.250	2	XX
595.417	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

105.00	357.00
140.00	370.00
178.00	370.00
200.00	384.00
213.00	394.00
235.00	410.00
238.00	440.00
259.00	454.00
262.00	465.00
280.00	520.00
280.00	640.00
291.00	
306.00	
310.00	
314.00	
320.00	
325.00	
325.00	
327.00	
327.00	
330.00	
340.00	
340.00	
350.00	
351.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES MET.	25
INCREMENT	372.00
MEAN	315.40
MEDIAN	329.00
SKEWNESS	.26
RANGE	467.00
VARIANCE	7493.00
STANDARD DEVIATION	86.64
95% CONF. (UPPER LIM.)	500.16
INTERVAL (LOWER LIM.)	133.44
COEF. OF VAR. (AS A %)	28.04
ACCURACY (% REL. ERR.)	-10.09

MIDPOINT FREQ. HISTOGRAM

178.700	4	XXXX
250.100	3	XXX
321.500	12	XXXXXXXXXXXX
392.900	3	XXX
464.300	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

143.00	
189.00	
200.00	
200.00	
237.00	
250.00	
261.00	
288.00	
300.00	
304.00	
313.00	
320.00	
324.00	
326.00	
327.00	
332.00	
340.00	
346.00	
347.00	
360.00	
370.00	
375.00	
480.00	
488.00	
500.00	

TABLE 6

Statistical Summary

Total Cyanide

by

Pyridine-Barbituric Acid Method

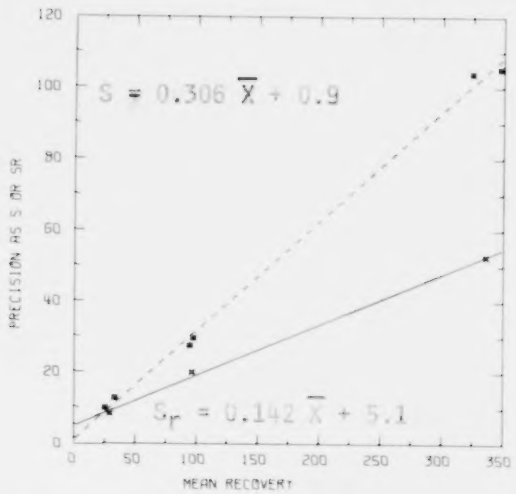
Statistical Parameters	Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul	
	1	3	1	3	4	5	4	5	6	2	6	2
True Value, µg/L	25	35	25	35	106	106	106	106	352	372	352	372
Values Retained	38	34	26	24	34	35	24	26	36	37	25	24
Mean Recovery, µg/L ($\bar{X}$)	26	34	25	37	95	98	89	86	326	349	317	345
Accuracy as % Rel. Error	2	-4	1	5	-11	-8	-16	-19	-8	-6	-10	-7
Std. Dev., µg/L (S)	10	13	13	20	27	29	20	45	104	105	89	100
Rel. Dev., %	38	38	50	56	29	30	23	52	32	30	28	29
Range, µg/L	41	60	47	80	103	152	75	242	535	488	357	417
Single-analyst Std. Dev., µg/L (S_r)	8.4		11.9		19.9		19.0		52.6		43.5	
Single-analyst Rel. Dev., %	28		38		21		22		16		13	

FIGURE 1

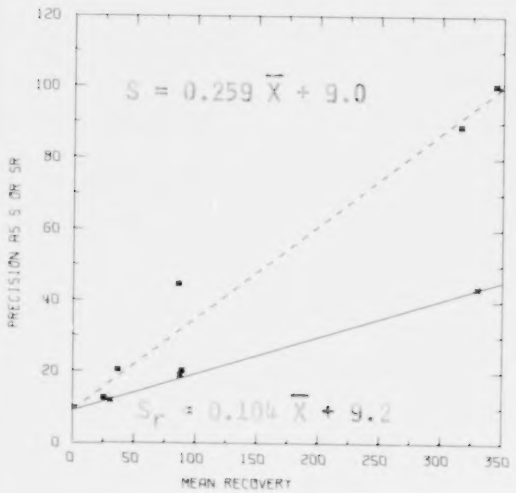
REGRESSION RESULTS FOR TOTAL CYANIDE
PYRIDINE-BARBITURIC ACID METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

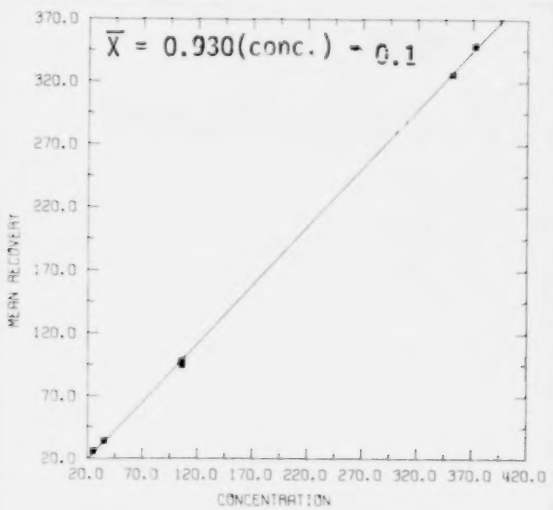


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

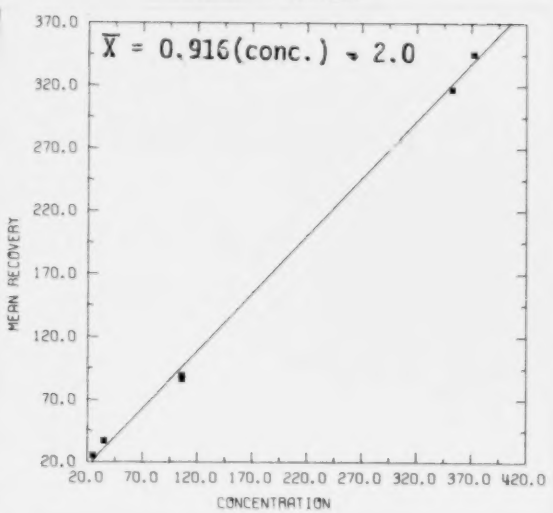
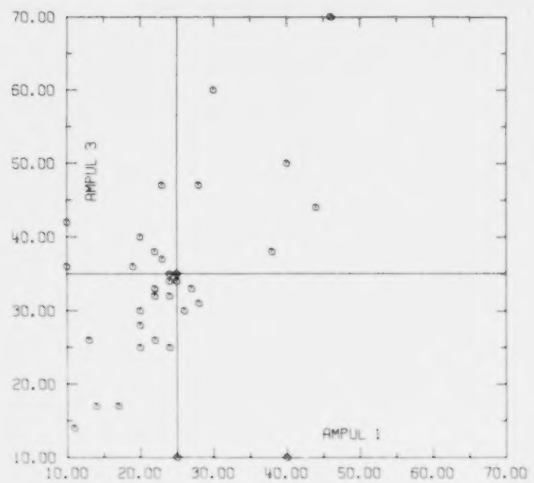


FIGURE 2

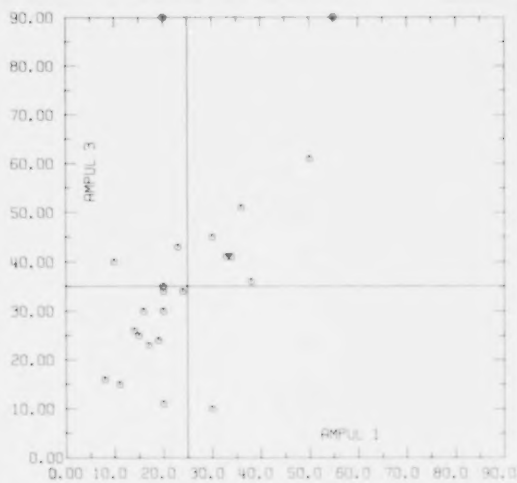
YOUDEN PLOTS FOR TOTAL CYANIDE
PYRIDINE-BARBITURIC ACID METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

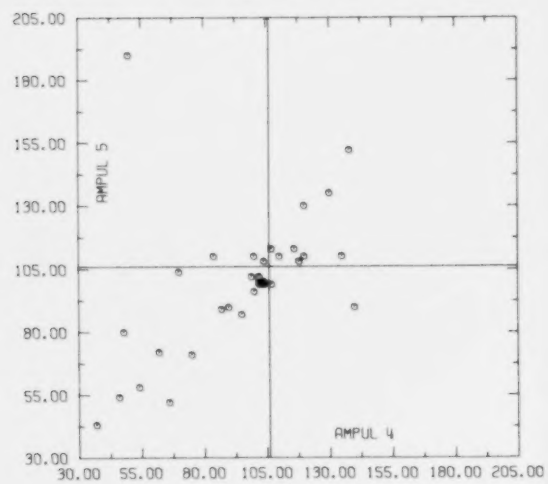


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

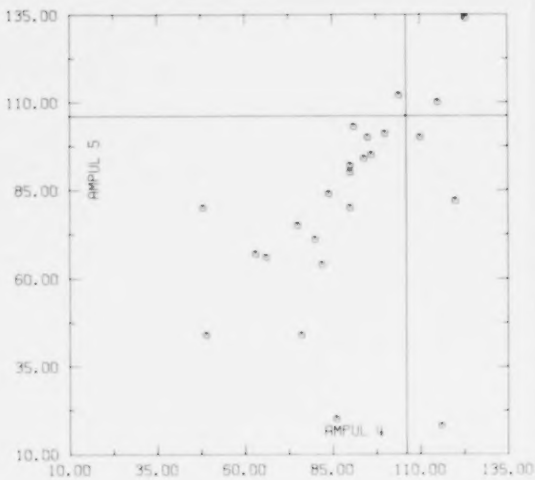
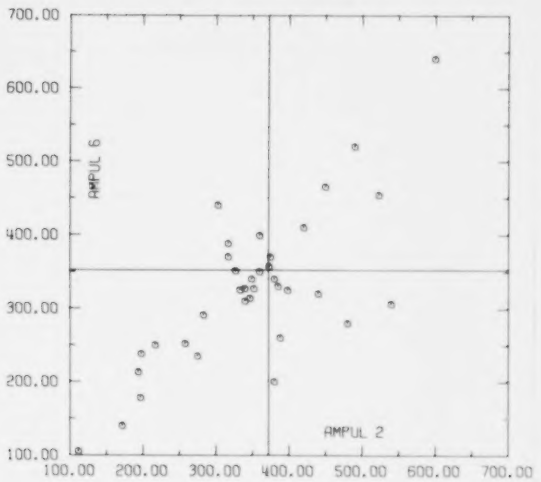


FIGURE 2
(continued)

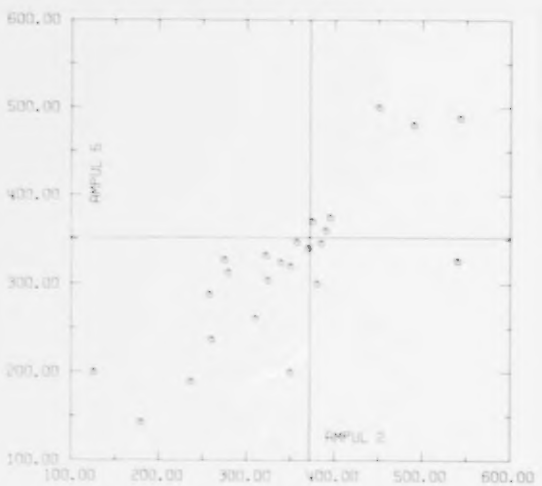
YOUDEN PLOTS FOR TOTAL CYANIDE
PYRIDINE-BARBITURIC ACID METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



Total Cyanide, Pyridine-Pyrazolone Method

Tables 7 and 8 show distilled water data and natural water data from sixteen and thirteen laboratories respectively. All data for one laboratory were rejected because the specified procedure was not followed. In addition, natural water data for three laboratories were rejected because the background levels were reported as "less than" values.

The histograms in Tables 9 through 11 for this method are quite different from those for the pyridine-barbituric method. There are no extreme high values such as those in the retained data for the pyridine-barbituric method. This may be because the participating analysts were more familiar with the pyridine-pyrazolone method. However, the histograms also show a clearer separation between analysts reporting more than 100 percent recovery and those reporting less. There are unexpectedly few analysts reporting data close to the true values. This lack of a strong central focus in the data is unusual, yet the pyridine pyrazolone method is acœptable; its statistics are similar to those for the pyridine-barbituric acid method.

The statistics summarized in Table 12 indicate no real difference between results from distilled and natural waters.

The pyridine-pyrazolone method is best characterized by the regression results in Figure 3. A comparison of these results and similar results for pyridine-barbituric (Figure 1) indicates the pyridine-pyrazolone method generated considerably less total variability (S), about the same single analyst variability (S_r) and slightly better mean recovery. If the difference between the total variability estimates can be explained by the inexperience of some participants in applying the pyridine-barbituric method, the data offer little difference between the methods.

The Youden plots in Figure 4 show the method characteristics noted above, but offer no additional insight.

TABLE 7

Raw Data for Total Cyanide

Pyridine-Pyrazolone Method

Recovery of Increment from Distilled Water

Increment In µg/L	Ampul 1 25.00	Ampul 2 372.00	Ampul 3 35.00	Ampul 4 106.00	Ampul 5 106.00	Ampul 6 352.00
Lab Code						
101	33.00	425.00	45.00	100.00	130.00	325.00
111		400.00	34.00	58.00	52.00	340.00
124	19.00	290.00	28.00	84.00	82.00	290.00
142	20.00	500.00	40.00	110.00	130.00	310.00
190		360.00	50.00	83.00	120.00	400.00
243	28.00	322.00	32.00	102.00	100.00	300.00
262	20.00	430.00	50.00	110.00	130.00	360.00
292	20.00	270.00	40.00	80.00	60.00	260.00
447	106.00*	458.00	127.00*	129.00	135.50	294.50
553	<40.00*	380.00	<40.00*	80.00	60.00	380.00
625	22.00	300.00	23.00	100.00	100.00	300.00
628	19.00	276.00	50.00	92.00	100.00	318.00
637	30.00	410.00	50.00	115.00	0.00	330.00
638	30.00	360.00	40.00	135.00	115.00	560.00*
650	188.00*IM	159.00*IM	94.00*IM	91.00*IM	91.00*IM	94.00*IM
651	10.00	400.00	15.00	130.00	100.00	285.00

* = Rejected
IM = Improper Method

TABLE 8

Raw Data for Total Cyanide

Pyridine-Pyrazolone Method

Recovery of Increment from Natural or Effluent Water

	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Increment In µg/L	25.00	372.00	35.00	106.00	106.00	352.00
Lab Code						
101	<28.00*	<330.00*	<37.00*	<110.00*	<110.00*	<350.00*
111		394.00	30.00	69.00	57.00	300.00
124	19.00	292.00	22.00	80.00	82.00	282.00
190		335.00	60.00	88.00	118.00	400.00
243	9.00	323.00	18.00	80.00	82.00	297.00
262	<20.00*	<410.00*	<50.00*	<110.00*	<140.00*	<390.00*
292	<30.00*	<370.00*	<40.00*	<100.00*	<110.00*	<350.00*
447	-58.50*	456.00	-8.50	47.00	131.50	375.50
625	21.00	280.00	20.00	98.00	98.00	300.00
628	184.00*	378.00	137.00*	149.00	139.00	336.00
638	28.00	400.00	40.00	140.00	116.00	560.00
650	-17.00*IM	353.00*IM	9.00*IM	0.00*IM	3.00*IM	22.00*IM
651	10.00	400.00	50.00	155.00		

* = Rejected
IM = Improper Method

TABLE 9

DATA SUMMARIES FOR TOTAL CYANIDE
PYRIDINE-PYRAZOLONE METHOD

LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	11
INCREMENT	25.00
MEAN	22.82
MEDIAN	20.00
SKEWNESS	-.10
RANGE	23.00
VARIANCE	45.16
STANDARD DEVIATION	6.72
95% CONF. (UPPER LIM.)	37.79
INTERVAL (LOWER LIM.)	7.86
COEF. OF VAR. (AS A %)	29.45
ACCURACY (% REL. ERR.)	-8.73

MIDPOINT	FREQ.	HISTOGRAM
13.833	1	X
21.500	6	XXXXXX
29.167	4	XXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

16.00	
19.00	
19.00	
20.00	
20.00	
20.00	
22.00	
26.00	
30.00	
30.00	
33.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	5
INCREMENT	25.00
MEAN	17.40
MEDIAN	19.00
SKEWNESS	.10
RANGE	19.00
VARIANCE	63.30
STANDARD DEVIATION	7.96
95% CONF. (UPPER LIM.)	39.49
INTERVAL (LOWER LIM.)	-4.69
COEF. OF VAR. (AS A %)	45.72
ACCURACY (% REL. ERR.)	-30.40

MIDPOINT	FREQ.	HISTOGRAM
13.750	2	XX
23.250	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

9.00
16.00
19.00
21.00
28.00

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	13
INCREMENT	35.00
MEAN	36.23
MEDIAN	40.00
SKEWNESS	-.56
RANGE	35.00
VARIANCE	128.53
STANDARD DEVIATION	11.34
95% CONF. (UPPER LIM.)	62.93
INTERVAL (LOWER LIM.)	13.53
COEF. OF VAR. (AS A %)	29.65
ACCURACY (% REL. ERR.)	9.23

MIDPOINT	FREQ.	HISTOGRAM
19.375	2	XX
28.125	2	XX
36.875	4	XXXX
45.625	5	XXXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

15.00	
23.00	
28.00	
32.00	
34.70	
40.00	
40.00	
40.00	
45.00	
50.00	
50.00	
50.00	
50.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	35.00
MEAN	28.94
MEDIAN	26.00
SKEWNESS	-.18
RANGE	68.50
VARIANCE	456.46
STANDARD DEVIATION	21.32
95% CONF. (UPPER LIM.)	74.35
INTERVAL (LOWER LIM.)	-21.47
COEF. OF VAR. (AS A %)	73.67
ACCURACY (% REL. ERR.)	-17.32

MIDPOINT	FREQ.	HISTOGRAM
2.917	1	X
25.750	4	XXXX
48.583	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-8.50
18.00
20.00
22.00
30.00
40.00
50.00
60.00

TABLE 10

DATA SUMMARIES FOR TOTAL CYANIDE PYRIDINE-PYRAZOLONE METHOD

MEDIUM CONCENTRATION PAIR

AMPUL 4

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	15
INCREMENT	106.00
MEAN	100.53
MEDIAN	100.00
SKEWNESS	-.07
RANGE	77.00
VARIANCE	468.84
STANDARD DEVIATION	21.65
95% CONF. (UPPER LIM.)	146.97
INTERVAL (LOWER LIM.)	54.09
COEF. OF VAR. (AS A %)	21.54
ACCURACY (% REL. ERR.)	-5.16

MIDPOINT	FREQ.	HISTOGRAM
67.625	1	X
86.875	5	XXXXX
106.125	6	XXXXXX
125.375	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

58.00	
80.00	
80.00	
83.00	
84.00	
92.00	
100.00	
100.00	
102.00	
110.00	
110.00	
115.00	
124.00	
130.00	
135.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	9
INCREMENT	106.00
MEAN	100.67
MEDIAN	88.00
SKEWNESS	.25
RANGE	104.00
VARIANCE	1467.50
STANDARD DEVIATION	38.31
95% CONF. (UPPER LIM.)	184.03
INTERVAL (LOWER LIM.)	17.33
COEF. OF VAR. (AS A %)	38.05
ACCURACY (% REL. ERR.)	-5.03

MIDPOINT	FREQ.	HISTOGRAM
65.000	4	XXXX
101.000	2	XX
137.000	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

47.00
64.00
80.00
88.00
88.00
88.00
140.00
149.00
155.00

AMPUL 5

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	15
INCREMENT	106.00
MEAN	94.30
MEDIAN	100.00
SKEWNESS	-.95
RANGE	135.50
VARIANCE	1423.28
STANDARD DEVIATION	37.73
95% CONF. (UPPER LIM.)	175.22
INTERVAL (LOWER LIM.)	13.38
COEF. OF VAR. (AS A %)	40.01
ACCURACY (% REL. ERR.)	-11.04

MIDPOINT	FREQ.	HISTOGRAM
16.937	1	X
50.813	3	XXX
84.687	5	XXXXX
118.562	6	XXXXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

.00
52.00
60.00
80.00
82.00
100.00
100.00
100.00
100.00
105.00
120.00
130.00
130.00
130.00
135.50

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	9
INCREMENT	106.00
MEAN	102.44
MEDIAN	107.00
SKEWNESS	-.22
RANGE	82.00
VARIANCE	784.32
STANDARD DEVIATION	28.00
95% CONF. (UPPER LIM.)	164.37
INTERVAL (LOWER LIM.)	36.50
COEF. OF VAR. (AS A %)	27.34
ACCURACY (% REL. ERR.)	-2.89

MIDPOINT	FREQ.	HISTOGRAM
70.667	3	XXX
88.000	1	X
125.333	4	XXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

57.00
82.00
82.00
88.00
116.00
118.00
131.50
134.00

TABLE 11

DATA SUMMARIES FOR TOTAL CYANIDE
PYRIDINE-PYRAZOLONE METHOD

HIGH CONCENTRATION PAIR

AMPUL 2

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	15
INCREMENT	372.00
MEAN	372.07
MEDIAN	380.00
SKEWNESS	.03
RANGE	230.00
VARIANCE	4810.35
STANDARD DEVIATION	69.36
95% CONF. (UPPER LIM.)	520.82
INTERVAL (LOWER LIM.)	223.31
COEF. OF VAR. (AS A %)	18.64
ACCURACY (% REL. ERR.)	.02

MIDPOINT	FREQ.	HISTOGRAM
298.750	5	XXXXX
356.250	3	XXX
413.750	5	XXXXX
471.250	2	XX

#RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

270.00
276.00
290.00
300.00
322.00
360.00
360.00
380.00
400.00
400.00
410.00
425.00
430.00
458.00
500.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	9
INCREMENT	372.00
MEAN	362.00
MEDIAN	378.00
SKEWNESS	.00
RANGE	176.00
VARIANCE	3454.75
STANDARD DEVIATION	57.96
95% CONF. (UPPER LIM.)	495.65
INTERVAL (LOWER LIM.)	228.34
COEF. OF VAR. (AS A %)	16.01
ACCURACY (% REL. ERR.)	-2.69

MIDPOINT	FREQ.	HISTOGRAM
309.333	4	XXXX
368.000	2	XX
426.667	3	XXX

#RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

285.00
292.00
321.00
335.00
378.00
394.00
450.00
460.00
461.00

AMPUL 6

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	14
INCREMENT	352.00
MEAN	320.89
MEDIAN	314.00
SKEWNESS	.53
RANGE	140.00
VARIANCE	1491.78
STANDARD DEVIATION	38.62
95% CONF. (UPPER LIM.)	404.34
INTERVAL (LOWER LIM.)	237.45
COEF. OF VAR. (AS A %)	12.04
ACCURACY (% REL. ERR.)	-6.84

MIDPOINT	FREQ.	HISTOGRAM
277.500	4	XXXX
312.500	5	XXXXX
347.500	3	XXX
382.500	2	XX

#RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

280.00
285.00
290.00
294.50
300.00
300.00
310.00
318.00
325.00
330.00
340.00
360.00
380.00
400.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	352.00
MEAN	327.21
MEDIAN	300.00
SKEWNESS	.53
RANGE	118.00
VARIANCE	2024.15
STANDARD DEVIATION	44.97
95% CONF. (UPPER LIM.)	437.33
INTERVAL (LOWER LIM.)	217.13
COEF. OF VAR. (AS A %)	13.75
ACCURACY (% REL. ERR.)	-7.04

MIDPOINT	FREQ.	HISTOGRAM
301.667	4	XXXX
341.000	1	X
380.333	2	XX

#RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

282.00
297.00
300.00
300.00
335.00
375.50
400.00

TABLE 12

Statistical Summary

Total Cyanide

by

Pyridine-Pyrazolone Method

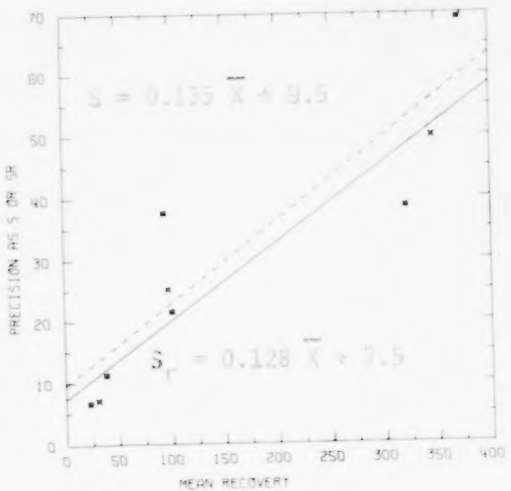
Statistical Parameters	Dist. Water Ampul 1	Dist. Water Ampul 3	Natrl. Water Ampul 1	Natrl. Water Ampul 3	Dist. Water Ampul 4	Dist. Water Ampul 5	Natrl. Water Ampul 4	Natrl. Water Ampul 5	Dist. Water Ampul 6	Dist. Water Ampul 2	Natrl. Water Ampul 6	Natrl. Water Ampul 2
True Value, µg/L	25	35	25	35	106	106	106	106	352	372	352	372
Values Retained	11	13	5	8	15	15	9	8	14	15	7	9
Mean Recovery, µg/L ($\bar{X}$)	23	38	17	29	101	94	101	103	321	372	327	362
Accuracy as % Rel. Error	-9	9	-30	-17	-5	-11	-5	-3	-9	0	-7	-3
Std. Dev., µg/L (S)	7	11	8	21	22	38	38	28	39	69	45	58
Rel. Dev., %	29	30	46	74	22	40	38	27	12	19	14	16
Range, µg/L	23	35	19	68	77	136	108	82	140	230	118	176
Single-analyst Std. Dev., µg/L (S_r)	7.2		11.4		25.3		24.2		50.0		39.2	
Single-analyst Rel. Dev., %	24		50		26		24		15		11	

FIGURE 3

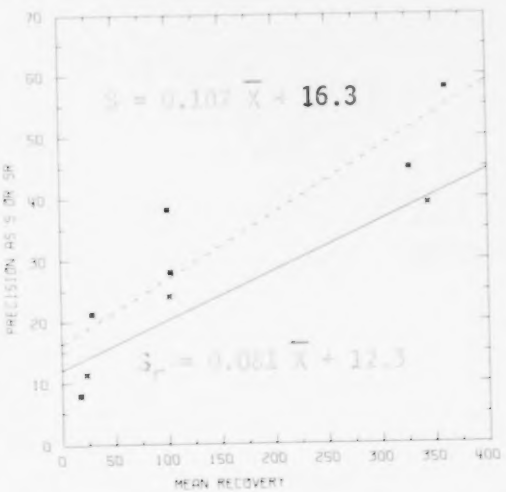
REGRESSION RESULTS FOR TOTAL CYANIDE
PYRIDINE-PYRAZOLONE METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

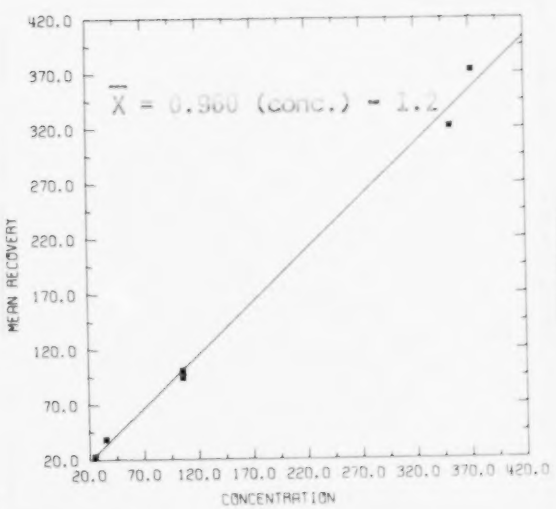


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

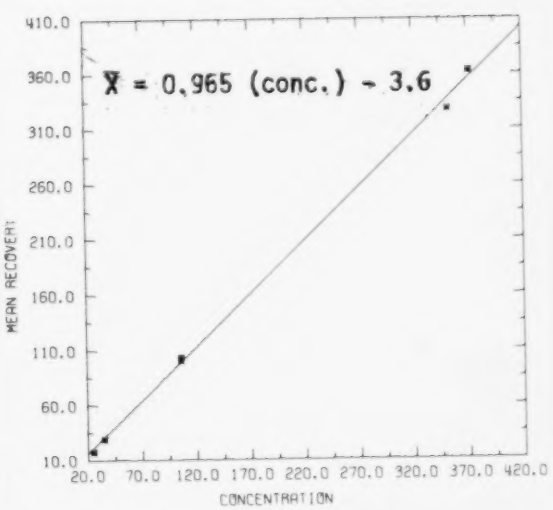
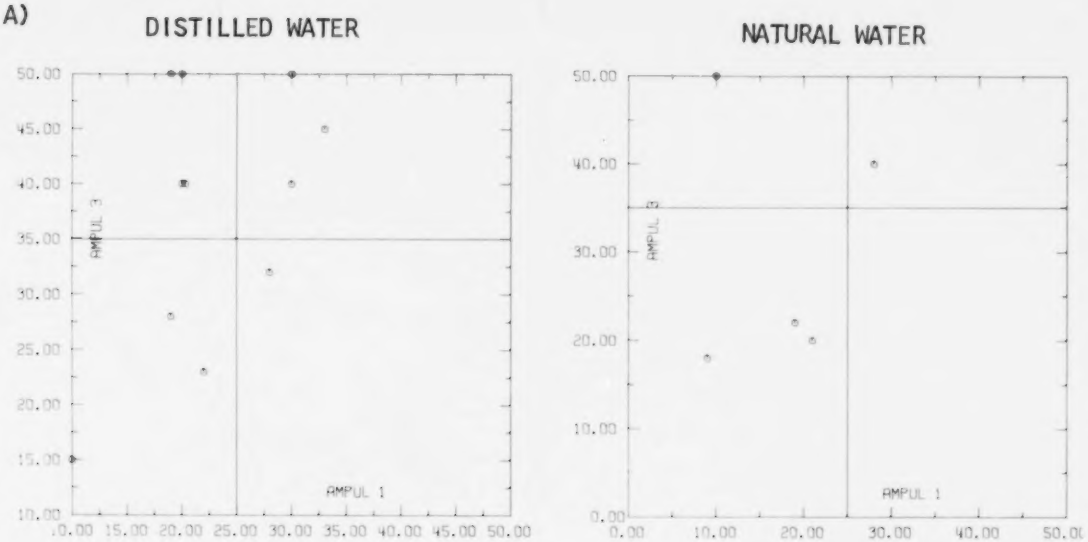


FIGURE 4

YOUDEN PLOTS FOR TOTAL CYANIDE
PYRIDINE-PYRAZOLONE METHOD

LOW CONCENTRATION PAIR IN UG/L

A)



MEDIUM CONCENTRATION PAIR IN UG/L

B)

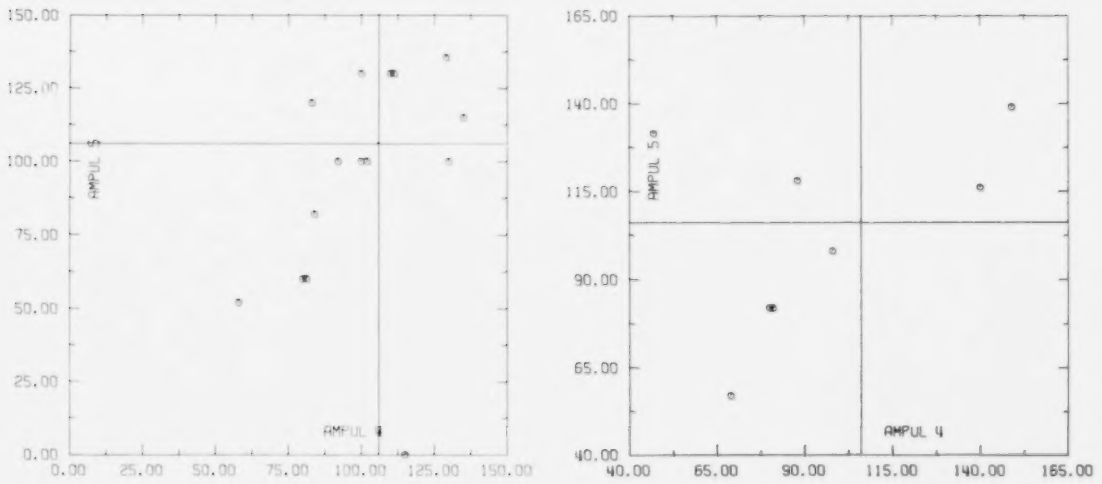
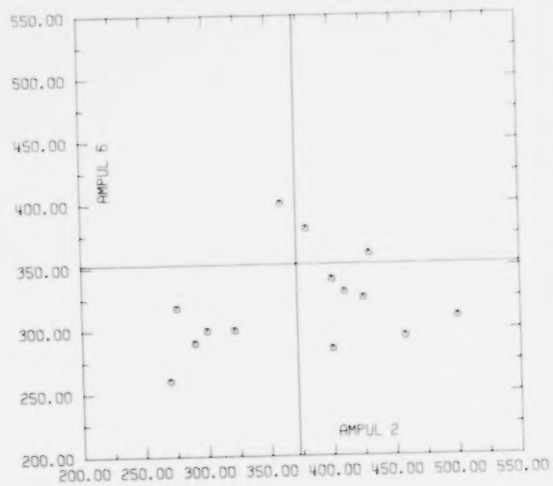


FIGURE 4
(continued)

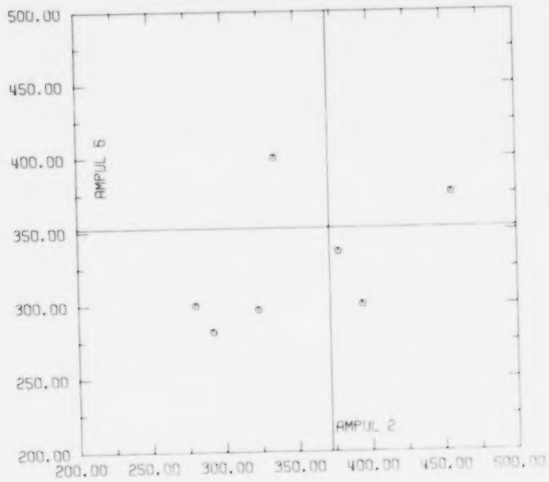
YOUDEN PLOTS FOR TOTAL CYANIDE
PYRIDINE-PYRAZOLONE METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



Total Cyanide, Electrode Method

In Tables 13 and 14, nine laboratories reported distilled water data and eight reported natural water data for the total cyanide electrode method. Natural water data from one of the laboratories were rejected because the background level was reported as a "less than" value.

Tables 15, 16 and 17 indicate that the mean and median recoveries exceeded the increment for distilled water analyses and for the natural water analyses at the low level. Much of this difference in mean recovery between the two types of water is apparently caused by laboratory 624, which reported high recoveries for all levels in distilled water, but did not report any natural water data.

Comparison of the standard deviations of natural and distilled water samples in Table 18 show no clear differences except at the low concentration level. The raw data in Table 14 show that many of the laboratories had systematic problems with the low concentration increments from the natural waters, i.e., results for both low concentration samples from a laboratory were generally either high or low. Since these systematic problems were low in some laboratories and high in others, the total standard deviation reflects the impact rather than mean recovery.

The regression results in Figure 5 support the hypothesis that the type of background water had no marked effect on the data. However, the precision plots show that the single analyst deviation (S_r) is unusually close to the total deviation (S). This suggests that the electrode method, over most of its range, is more sensitive to the random errors than it is to systematic differences between laboratories, such as differences in reagent, instrument, and analyst.

Comparisons of the electrode method statistics in Table 18 with statistics for the colorimetric methods in Tables 6 and 12 show that the mean recovery was less stable and both S and S_r were larger for the electrode method. The electrode method regressions in Figure 5, when compared with the comparable regressions for the colorimetric methods in Figures 1 and 3, provide visual support for the proceeding conclusions. The electrode method obviously produced the largest variance estimates and, through the greater distance between the points and the lines in its accuracy plots, it is clear that mean recovery for the electrode method was less stable.

The limited data in Youden Plots presented in Figure 6 offer no additional insight into this method's characteristics.

TABLE 13

Raw Data for Total Cyanide

Electrode Method

Recovery of Increment from Distilled Water

Increment In µg/L	Ampul 1 25.00	Ampul 2 372.00	Ampul 3 35.00	Ampul 4 106.00	Ampul 5 106.00	Ampul 6 352.00
Lab Code						
292	40.00	390.00	30.00	160.00	600.00*	390.00
438	25.00	310.00	39.00	73.00	90.00	260.00
624	50.00	600.00	30.00	200.00	200.00	560.00
627	26.00	980.00*	77.00	250.00	222.00	660.00
631	23.00	300.00	19.00	92.00	100.00	321.00
634	30.00	390.00	46.00	120.00	90.00	400.00
635	48.00	503.00	30.00	93.00	78.00	238.00
638	30.00	360.00	40.00	135.00	115.00	560.00
642	26.00	300.00	42.00	114.00	128.00	420.00

* = Rejected

TABLE 14

Raw Data for Total Cyanide

Electrode Method

Recovery of Increment from Natural or Effluent Water

Increment In ug/L	Ampul 1 25.00	Ampul 2 372.00	Ampul 3 35.00	Ampul 4 106.00	Ampul 5 106.00	Ampul 6 352.00
Lab Code						
292	<40.00*	<650.00*	<60.00*	<160.00*	<180.00*	<580.00*
438	-5.00	307.00	14.00	39.00	87.00	297.00
627	80.00	984.00*	78.00	250.00	260.00*	660.00
631	180.00	360.00	1040.00*	30.00	60.00	270.00
634	27.00	400.00	44.00		80.00	350.00
635	-29.00	305.00	12.00	-1.00	13.00	170.00
638	28.00	400.00	40.00	140.00	116.00	560.00
642	16.00	274.00	80.00	100.00	110.00	456.00

* = Rejected

TABLE 15

DATA SUMMARIES FOR TOTAL CYANIDE ELECTRODE METHOD

LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	9
INCREMENT	25.00
MEAN	33.11
MEDIAN	30.00
SKEWNESS	.63
RANGE	27.00
VARIANCE	105.36
STANDARD DEVIATION	10.26
95% CONF. (UPPER LIM.)	46.78
INTERVAL (LOWER LIM.)	9.44
COEF. OF VAR. (AS A %)	31.00
ACCURACY (% REL. ERR.)	32.44

MIDPOINT FREQ. HISTOGRAM

27.50	6	XXXXXX
36.500	1	X
45.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

23.00
25.00
26.00
26.00
30.00
30.00
40.00
48.00
50.00

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	7
INCREMENT	25.00
MEAN	42.43
MEDIAN	27.00
SKEWNESS	.93
RANGE	209.00
VARIANCE	4805.62
STANDARD DEVIATION	69.32
95% CONF. (UPPER LIM.)	212.05
INTERVAL (LOWER LIM.)	-127.20
COEF. OF VAR. (AS A %)	163.39
ACCURACY (% REL. ERR.)	99.71

MIDPOINT FREQ. HISTOGRAM

5.833	5	XXXXX
75.500	1	X
145.167	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-29.00
-5.00
15.00
27.00
25.00
80.00
180.00

AMPUL 3

B) DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	9
INCREMENT	35.00
MEAN	44.78
MEDIAN	40.00
SKEWNESS	.66
RANGE	81.00
VARIANCE	430.69
STANDARD DEVIATION	20.75
95% CONF. (UPPER LIM.)	92.63
INTERVAL (LOWER LIM.)	-3.08
COEF. OF VAR. (AS A %)	46.35
ACCURACY (% REL. ERR.)	27.94

MIDPOINT FREQ. HISTOGRAM

29.167	4	XXXX
64.500	3	XXX
69.833	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

19.00
30.00
40.00
44.00
60.00
42.00
46.00
77.00
80.00

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	6
INCREMENT	35.00
MEAN	44.67
MEDIAN	42.00
SKEWNESS	.11
RANGE	68.00
VARIANCE	477.87
STANDARD DEVIATION	24.63
95% CONF. (UPPER LIM.)	120.85
INTERVAL (LOWER LIM.)	-31.50
COEF. OF VAR. (AS A %)	66.33
ACCURACY (% REL. ERR.)	27.62

MIDPOINT FREQ. HISTOGRAM

29.000	4	XXXX
63.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

12.00
14.00
40.00
44.00
78.00
80.00

TABLE 16

DATA SUMMARIES FOR TOTAL CYANIDE ELECTRODE METHOD

MEDIUM CONCENTRATION PAIR

AMPUL 4

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	9
INCREMENT	106.00
MEAN	137.44
MEDIAN	120.00
SKEWNESS	.72
RANGE	177.00
VARIANCE	3268.03
STANDARD DEVIATION	57.17
95% CONF. (UPPER LIM.)	264.27
INTERVAL (LOWER LIM.)	5.62
COEF. OF VAR. (AS A %)	41.59
ACCURACY (% REL. ERR.)	24.05

MIDPOINT	FREQ.	HISTOGRAM
102.500	5	XXXXX
161.500	2	XX
220.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

75.00	
92.00	
93.00	
114.00	
120.00	
135.00	
160.00	
200.00	
252.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	106.00
MEAN	93.00
MEDIAN	69.50
SKEWNESS	.58
RANGE	251.00
VARIANCE	8525.60
STANDARD DEVIATION	92.33
95% CONF. (UPPER LIM.)	330.35
INTERVAL (LOWER LIM.)	-144.35
COEF. OF VAR. (AS A %)	99.28
ACCURACY (% REL. ERR.)	-12.26

MIDPOINT	FREQ.	HISTOGRAM
61.750	4	XXXX
167.250	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-1.00
30.00
34.00
100.00
140.00
250.00

AMPUL 5

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	106.00
MEAN	127.87
MEDIAN	107.50
SKEWNESS	.76
RANGE	144.00
VARIANCE	2408.70
STANDARD DEVIATION	53.93
95% CONF. (UPPER LIM.)	255.40
INTERVAL (LOWER LIM.)	.35
COEF. OF VAR. (AS A %)	42.18
ACCURACY (% REL. ERR.)	20.04

MIDPOINT	FREQ.	HISTOGRAM
102.000	5	XXXXX
150.000	1	X
198.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

78.00
90.00
90.00
100.00
115.00
122.00
200.00
222.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	106.00
MEAN	77.67
MEDIAN	83.50
SKEWNESS	-.58
RANGE	103.00
VARIANCE	1420.27
STANDARD DEVIATION	37.69
95% CONF. (UPPER LIM.)	174.54
INTERVAL (LOWER LIM.)	-19.21
COEF. OF VAR. (AS A %)	48.52
ACCURACY (% REL. ERR.)	-26.73

MIDPOINT	FREQ.	HISTOGRAM
38.750	2	XX
90.250	4	XXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

13.00
60.00
80.00
87.00
110.00
116.00

TABLE 17

DATA SUMMARIES FOR TOTAL CYANIDE ELECTRODE METHOD

HIGH CONCENTRATION PAIR

AMPUL 2

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	372.00
MEAN	394.12
MEDIAN	375.00
SKEWNESS	.79
RANGE	300.00
VARIANCE	11461.84
STANDARD DEVIATION	107.06
95% CONF. (UPPER LIM.)	647.28
INTERVAL (LOWER LIM.)	140.97
COEF. OF VAR. (AS A %)	27.16
ACCURACY (% REL. ERR.)	5.95

MIDPOINT	FREQ.	HISTOGRAM
350.000	6	XXXXXX
450.000	0	
550.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

300.00
300.00
310.00
360.00
390.00
390.00
503.00
600.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	372.00
MEAN	341.00
MEDIAN	333.50
SKEWNESS	.03
RANGE	126.00
VARIANCE	2852.80
STANDARD DEVIATION	53.41
95% CONF. (UPPER LIM.)	478.30
INTERVAL (LOWER LIM.)	203.70
COEF. OF VAR. (AS A %)	15.66
ACCURACY (% REL. ERR.)	-8.33

MIDPOINT	FREQ.	HISTOGRAM
305.500	3	XXX
368.500	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

274.00
305.00
307.00
360.00
400.00
400.00

AMPUL 6

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	9
INCREMENT	352.00
MEAN	423.22
MEDIAN	400.00
SKEWNESS	.24
RANGE	422.00
VARIANCE	20816.45
STANDARD DEVIATION	144.28
95% CONF. (UPPER LIM.)	755.93
INTERVAL (LOWER LIM.)	90.51
COEF. OF VAR. (AS A %)	34.09
ACCURACY (% REL. ERR.)	20.23

MIDPOINT	FREQ.	HISTOGRAM
308.333	3	XXX
449.000	3	XXX
589.667	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

238.00
260.00
321.00
390.00
400.00
420.00
560.00
560.00
660.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	352.00
MEAN	394.71
MEDIAN	350.00
SKEWNESS	.25
RANGE	490.00
VARIANCE	29841.57
STANDARD DEVIATION	172.75
95% CONF. (UPPER LIM.)	817.41
INTERVAL (LOWER LIM.)	-27.98
COEF. OF VAR. (AS A %)	43.77
ACCURACY (% REL. ERR.)	12.13

MIDPOINT	FREQ.	HISTOGRAM
251.667	3	XXX
415.000	2	XX
578.333	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

170.00
270.00
297.00
350.00
456.00
560.00
660.00

TABLE 18

Statistical Summary

Total Cyanide

by

Electrode Method

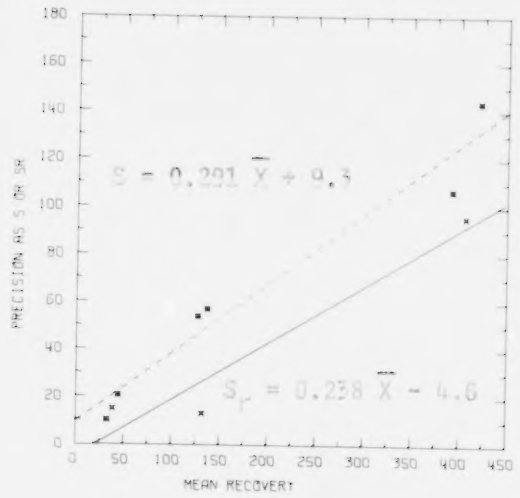
Statistical Parameters	Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul	
	1	3	1	3	4	5	4	5	6	2	6	2
True Value, µg/L	25	35	25	35	106	106	106	106	352	372	352	372
Values Retained	9	9	7	6	9	8	6	6	9	8	7	6
Mean Recovery, µg/L ($\bar{X}$)	33	45	42	45	137	128	93	78	423	394	395	341
Accuracy as % Rel. Error	32	28	70	28	30	21	-12	-27	20	6	12	-8
Std. Dev., µg/L (S)	10	21	69	30	57	54	92	38	144	107	173	53
Rel. Dev., %	31	46	163	66	42	42	99	49	34	27	44	16
Range, µg/L	27	61	209	68	177	144	251	103	422	300	490	126
Single-analyst Std. Dev., µg/L (S_r)	15		17		13		19		96		93	
Single-analyst Rel. Dev., %	38		38		10		22		24		25	

FIGURE 5

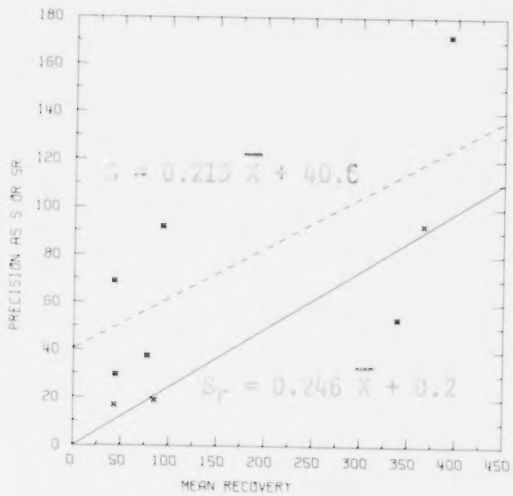
REGRESSION RESULTS FOR TOTAL CYANIDE
ELECTRODE METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

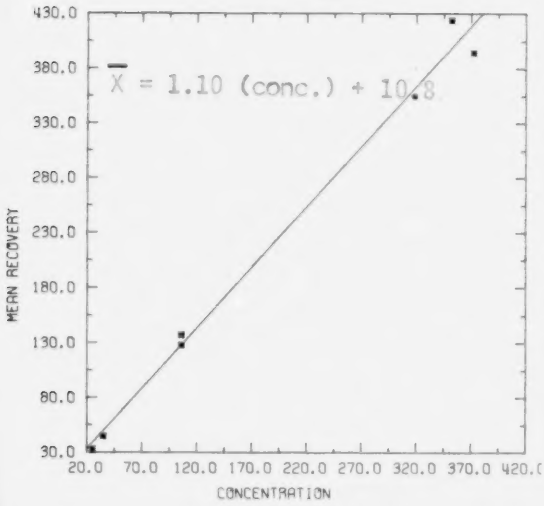


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

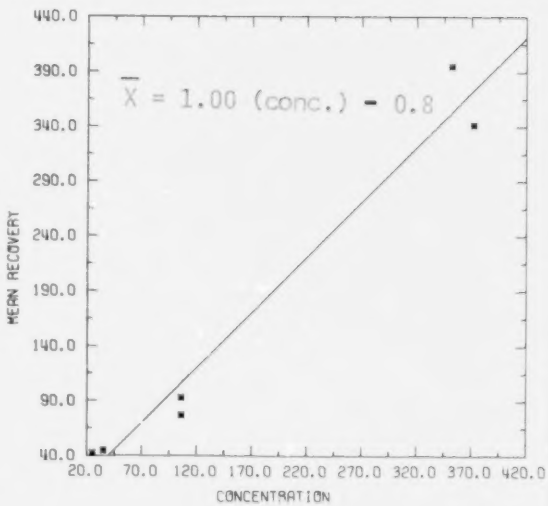
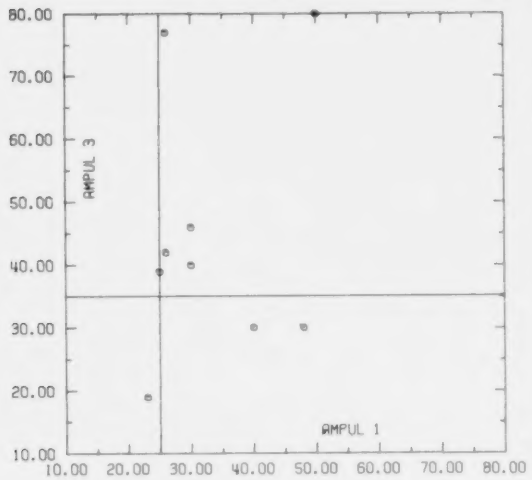


FIGURE 6

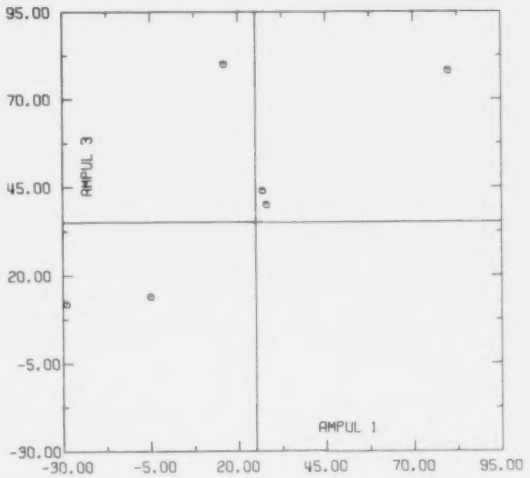
YOUDEN PLOTS FOR TOTAL CYANIDE
ELECTRODE METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

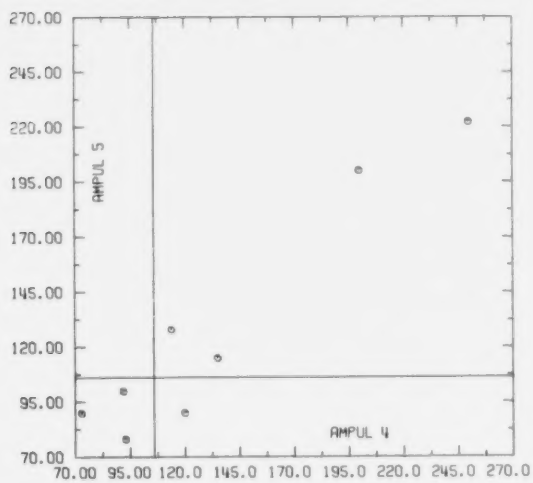


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

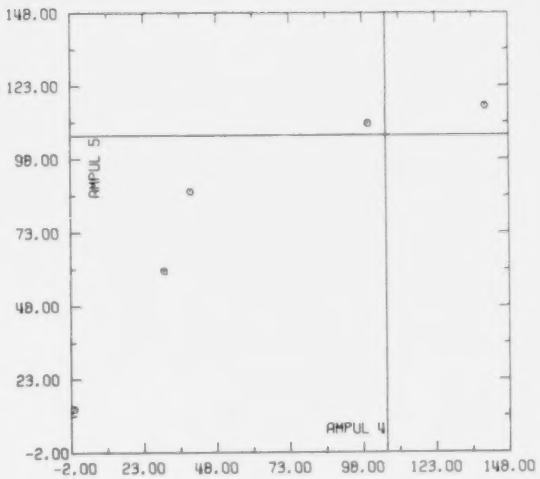


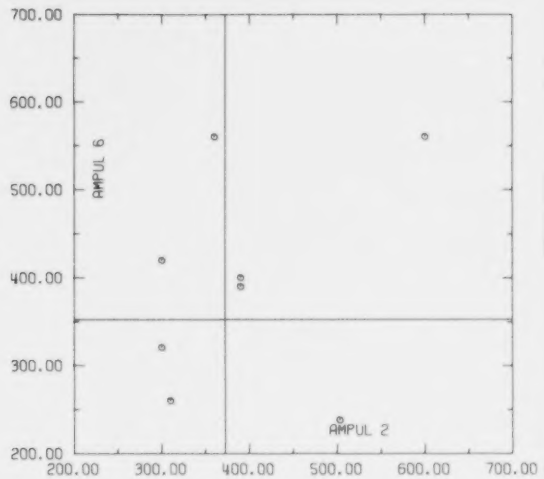
FIGURE 6
(continued)

YOUDEN PLOTS FOR TOTAL CYANIDE
ELECTRODE METHOD

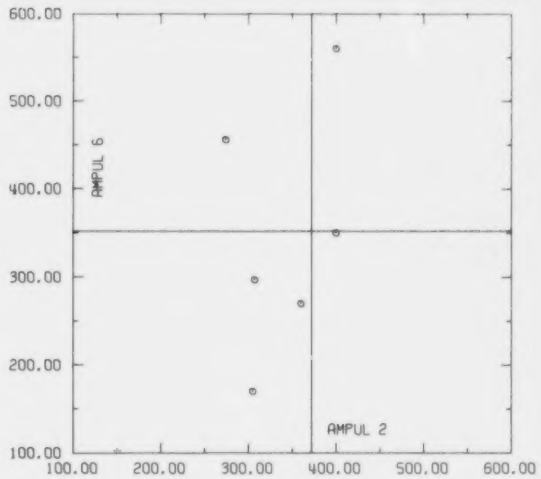
HIGH CONCENTRATION PAIR IN UG/L

C)

DISTILLED WATER



NATURAL WATER



Summary for Total Cyanide in Natural Waters

The mean recoveries ($\bar{X}$), overall standard deviations (S) and single analyst standard deviations (S_r) for natural water analyses by each of the methods within the concentration range 25-400 µg/liter, are as follows.

Method	$\bar{X}$	S	S_r
P-B*	0.916 (conc.) - 2.0	0.259 $\bar{X}$ + 9.0	0.104 $\bar{X}$ + 9.2
P-P**	0.965 (conc.) - 3.6	0.107 $\bar{X}$ + 16.3	0.081 $\bar{X}$ + 12.3
Electrode	1.00 (conc.) - 0.8	0.213 $\bar{X}$ + 40.6	0.246 $\bar{X}$ + 0.2

At the extremes of the applicable range, these equations lead to the following statistical estimates in µg/liter.

	25 µg/liter Level			400 µg/liter Level		
Method	$\bar{X}$	S	S_r	$\bar{X}$	S	S_r
P-B*	20.9	15.5	11.8	364.4	112.6	50.8
P-P**	20.5	19.0	14.3	382.4	59.1	44.7
Electrode	24.2	45.9	6.3	399.2	125.8	98.6

* Pyridine-barbituric Acid
** Pyridine-pyrazolone

These tables make the larger variability of the electrode method obvious and, although fortuitous averaging makes its mean recovery look better, recall that its mean recoveries were much more variable. Between the colorimetric methods, the apparent statistical advantage of the pyridine-pyrazolone method is also quite clear.

Cyanide Amenable to Chlorination, General Observations

The parameter, cyanide amenable to chlorination (CATC), employs a chlorination procedure to discriminate between free and complexed cyanides or in a broader sense, to distinguish between toxic and non-toxic cyanides. In CATC, a sample containing simple and complexed cyanides is first treated

with free chlorine until a chlorine residual is reached. The simple cyanides are converted to nitrogen gas and carbonate and the remaining complexed cyanides are converted to simple cyanide by acidification, then distilled, absorbed and measured. Total cyanide is also measured on an untreated aliquot of sample and the difference between cyanides before and after chlorination is termed cyanide amenable to chlorination. Since thedetermination is based on the difference between two colorimetric measurements, one might predict that the parameter would be less precise than a single measurement for total cyanide.

CATC, Pyridine-Barbituric Acid Method

In Tables 19 and 20, thirty-two laboratories reported distilled water data and thirty-one reported natural water data. Natural water data from five laboratories were rejected because the background levels were reported as "less than" values. The empty cells and secondary peaks in some histograms of Tables 21-23 suggest that outliers persisted in the data.

The statistics in Table 24 indicate the method was affected by natural waters. In particular, the relative deviations and single analyst relative deviations are consistently larger for the natural water samples than for distilled water samples. The differences in relative deviation of distilled and natural water samples decreased as the concentration increased and most of the relative deviation for the low concentration pair in natural water can be attributed to single analyst deviation. Analysts had problems obtaining consistent results for the low concentration pair in natural water.

Part A of Figure 7 clearly illustrates the effect of natural water matrices on results from the P-B method. At low concentration levels, the single analyst deviation (S_r) was twice as large in natural water as it was in distilled water. At higher concentration levels, the single analyst deviations were similar for both water types. The overall standard deviation (S) was about 50 percent larger in natural water than in distilled water for all levels.

The Youden plots in Figure 8 indicate that a few outliers are present in the retained data. These divergent points are most obvious in the plots of distilled water data for the high concentration pair and natural water data at all concentration levels.

TABLE 19

Raw Data for Cyanide Amenable to Chlorination

Pyridine-Barbituric Acid Method

Recovery of Increment from Distilled Water

	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Increment In µg/L	13.00	149.00	18.00	64.00	64.00	141.00
Lab Code						
102	20.00	210.00	30.00	50.00	50.00	140.00
110	28.00	125.00	8.00	20.00	39.00	134.00
112	13.00	143.00	35.00	90.00	98.00	288.00
138	28.00	318.00	42.00	76.00	66.00	104.00
157	25.00	395.00	10.00	35.00	32.00	332.00
167	8.00	117.00	16.00	55.00	55.00	171.00
197	10.00	110.00	20.00	61.00	63.00	135.00
204	17.00	215.00	15.00	68.00	62.00	99.00
259	22.00	149.00	15.00	85.00	65.00	148.00
388	15.00		33.00	90.00	130.00	236.00
438	12.00	48.00	36.00	60.00	43.00	104.00
566	5.00	220.00	10.00	30.00	30.00	170.00
572	20.00	184.00	17.00	49.00		
624	<10.00*	160.00	10.00	40.00	30.00	160.00
626	19.00	228.00	15.00	74.00	63.00	160.00
627	35.00	481.00*	55.00	195.00	200.00*	290.00
629	35.00	250.00	60.00*	50.00	50.00	20.00
630	6.00	208.00	15.00	32.00	36.00	200.00
631	8.00	171.00	17.00	60.00	60.00	130.00
632	11.00	113.00	12.00	56.00	44.00	99.00
633	30.00	61.00	164.00*	258.00*	168.00	107.00
635	14.00	231.00	32.00	105.00	72.00	189.00
636		88.00				
639	14.00	164.00	20.00	67.00	62.00	147.00
641	14.00	227.00	15.00		30.00	187.00
643	<5.00*	186.00	<5.00*	<5.00*	<5.00*	175.00
644	11.00	160.00	17.00	62.00	60.00	180.00
645	<10.00*	204.00	20.00	44.00	44.00	204.00
646	<10.00*	167.00	17.00	33.00	25.00	171.00
647	7.00	78.00	15.00	59.00	66.00	115.00
648	12.00	128.00	20.00	64.00	39.00	133.00
649	13.00	250.00	26.00	90.00	90.00	210.00

* = Rejected

TABLE 20

Raw Data for Cyanide Amenable to Chlorination

Pyridine-Barbituric Acid Method

Recovery of Increment from Natural or Effluent Water

Increment In µg/L	Ampul 1 13.00	Ampul 2 149.00	Ampul 3 18.00	Ampul 4 64.00	Ampul 5 64.00	Ampul 6 141.00
Lab Code						
102	0.00	220.00	10.00	40.00	40.00	120.00
110	33.00	145.00	20.00	36.00	63.00	159.00
112		<170.00*	<30.00*		<20.00*	<130.00*
122	7.00	97.00	10.00	66.00	58.00	123.00
138	30.00	340.00	30.00	50.00	62.00	127.00
157	30.00	420.00	10.00	35.00	32.00	397.00
167	10.00	140.00	18.00	57.00	55.00	135.00
204	-20.00	130.00	34.00	-4.00	-63.00	82.00
211	11.00		15.00		56.00	
259				<56.00*	<50.00*	<140.00*
388	32.00	30.00	41.00	123.00	134.00	109.00
438	-62.00*	95.00	25.00	16.00	6.00	130.00
566	5.00	220.00	5.00	30.00	30.00	195.00
572	14.00	141.00	-366.00*	<42.00*		
626	5.00	170.00		46.00	2.00	180.00
627		504.00	55.00	210.00*	235.00	300.00
629	10.00	230.00	70.00	60.00	40.00	30.00
630	5.00	185.00	12.00	32.00	33.00	195.00
631	-8.00	81.00	-60.00	-38.00	82.00	16.00
632	11.00	77.00	11.00	31.00	28.00	74.00
633	23.00	12.00	93.00	248.00*	185.00	48.00
635	15.00	211.00	10.00	42.00	0.00	225.00
636		<134.00*				
639	-3.00	236.00	88.00	175.00*	232.00	217.00
640	10.00	200.00	10.00	50.00	80.00	150.00
641	<13.00*	<224.00*	<5.00*	<60.00*	<40.00*	<192.00*
644	10.00	170.00	20.00	60.00	58.00	160.00
646	-4.00	<225.00*	50.00	21.00	13.00	121.00
647	<6.00*	<101.00*	<13.00*	<62.00*	<74.00*	<127.00*
648	-5.00	51.00	8.00	44.00	46.00	81.00
649	14.00	274.00	26.00	74.00	74.00	274.00

* = Rejected

TABLE 21

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION PYRIDINE-BARBITURIC ACID METHOD LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	27
INCREMENT	13.00
MEAN	16.74
MEDIAN	14.00
SKEWNESS	.69
RANGE	30.00
VARIANCE	74.20
STANDARD DEVIATION	8.61
95% CONF. (UPPER LIM.)	34.45
INTERVAL (LOWER LIM.)	-.97
COEF. OF VAR. (AS A %)	51.45
ACCURACY (% REL. ERR.)	28.77

MIDPOINT	FREQ.	HISTOGRAM
8.000	6	XXXXXX
14.000	10	XXXXXXXXXX
20.000	5	XXXXX
26.000	3	XXX
32.000	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

5.00	35.00
6.00	35.00
7.00	
8.00	
8.00	
10.00	
11.00	
11.00	
12.00	
12.00	
13.00	
13.00	
14.00	
14.00	
14.00	
15.00	
17.00	
19.00	
20.00	
20.00	
22.00	
25.00	
28.00	
28.00	
30.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	24
INCREMENT	13.00
MEAN	4.79
MEDIAN	10.00
SKEWNESS	.02
RANGE	53.00
VARIANCE	175.56
STANDARD DEVIATION	13.25
95% CONF. (UPPER LIM.)	37.20
INTERVAL (LOWER LIM.)	-17.62
COEF. OF VAR. (AS A %)	135.32
ACCURACY (% REL. ERR.)	-24.68

MIDPOINT	FREQ.	HISTOGRAM
-14.700	1	X
-4.100	5	XXXXX
6.500	10	XXXXXXXXXX
17.100	3	XXX
27.700	5	XXXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-20.00
-8.00
-5.00
-4.00
-3.00
.00
5.00
5.00
5.00
7.00
10.00
10.00
10.00
10.00
11.00
11.00
14.00
14.00
15.00
23.00
30.00
30.00
32.00
33.00

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	28
INCREMENT	18.00
MEAN	21.18
MEDIAN	17.00
SKEWNESS	1.27
RANGE	47.00
VARIANCE	122.60
STANDARD DEVIATION	11.07
95% CONF. (UPPER LIM.)	43.98
INTERVAL (LOWER LIM.)	-1.56
COEF. OF VAR. (AS A %)	52.28
ACCURACY (% REL. ERR.)	17.66

MIDPOINT	FREQ.	HISTOGRAM
12.700	16	XXXXXXXXXXXXXXXX
22.100	5	XXXXX
31.500	5	XXXXX
40.900	1	X
50.300	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

8.00	36.00
10.00	42.00
15.00	55.00
16.00	
12.00	
15.00	
15.00	
15.00	
15.00	
15.00	
15.00	
16.00	
17.00	
17.00	
17.00	
17.00	
20.00	
20.00	
20.00	
20.00	
26.00	
30.00	
32.00	
33.00	
35.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	24
INCREMENT	18.00
MEAN	25.46
MEDIAN	19.00
SKEWNESS	.03
RANGE	153.00
VARIANCE	961.04
STANDARD DEVIATION	31.00
95% CONF. (UPPER LIM.)	89.59
INTERVAL (LOWER LIM.)	-38.67
COEF. OF VAR. (AS A %)	121.77
ACCURACY (% REL. ERR.)	41.44

MIDPOINT	FREQ.	HISTOGRAM
-44.700	1	X
-14.100	0	
16.500	16	XXXXXXXXXXXXXXXX
47.100	4	XXXX
77.700	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-60.00
5.00
8.00
10.00
10.00
10.00
10.00
10.00
11.00
12.00
15.00
18.00
20.00
20.00
25.00
26.00
30.00
34.00
41.00
50.00
55.00
70.00
88.00
93.00

TABLE 22

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION PYRIDINE-BARBITURIC ACID METHOD MEDIUM CONCENTRATION PAIR

A) AMPUL 4

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	28
INCREMENT	6*.00
MEAN	6*.29
MEDIAN	60.00
SKEWNESS	2.11
RANGE	175.00
VARIANCE	1085.32
STANDARD DEVIATION	32.96
95% CONF. (UPPER LIM.)	131.88
INTERVAL (LOWER LIM.)	-3.31
COEF. OF VAR. (AS A %)	51.25
ACCURACY (% REL. ERR.)	.65

MIDPOINT FREQ. HISTOGRAM

37.500	10	XXXXXXXXXX
72.500	13	XXXXXXXXXXXXX
107.500	4	XXXX
142.500	0	
177.500	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

20.00	90.00
30.00	105.00
32.00	195.00
33.00	
35.00	
40.00	
44.00	
49.00	
50.00	
50.00	
55.00	
56.00	
59.00	
60.00	
60.00	
61.00	
62.00	
64.00	
67.00	
68.00	
74.00	
76.00	
85.00	
90.00	
90.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	21
INCREMENT	6*.00
MEAN	41.48
MEDIAN	42.00
SKEWNESS	-.05
RANGE	161.00
VARIANCE	963.15
STANDARD DEVIATION	31.03
95% CONF. (UPPER LIM.)	106.21
INTERVAL (LOWER LIM.)	-23.26
COEF. OF VAR. (AS A %)	74.83
ACCURACY (% REL. ERR.)	-35.19

MIDPOINT FREQ. HISTOGRAM

-21.500	1	X
10.500	4	XXX
42.500	12	XXXXXXXXXXX
74.500	4	XXXX
106.500	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-18.00	
-8.00	
16.00	
21.00	
30.00	
31.00	
32.00	
35.00	
36.00	
40.00	
42.00	
44.00	
45.00	
50.00	
50.00	
57.00	
60.00	
60.00	
66.00	
74.00	
123.00	

B) AMPUL 5

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	28
INCREMENT	6*.00
MEAN	59.71
MEDIAN	57.50
SKEWNESS	1.77
RANGE	143.00
VARIANCE	976.51
STANDARD DEVIATION	31.25
95% CONF. (UPPER LIM.)	123.81
INTERVAL (LOWER LIM.)	-4.40
COEF. OF VAR. (AS A %)	52.33
ACCURACY (% REL. ERR.)	-6.70

MIDPOINT FREQ. HISTOGRAM

39.300	13	XXXXXXXXXXXXX
67.900	11	XXXXXXXXXXX
96.500	2	XX
125.100	1	X
153.700	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

25.00	98.00
30.00	130.00
30.00	168.00
30.00	
32.00	
35.00	
39.00	
39.00	
43.00	
44.00	
44.00	
50.00	
50.00	
55.00	
60.00	
60.00	
62.00	
62.00	
63.00	
63.00	
65.00	
65.00	
66.00	
72.00	
90.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	25
INCREMENT	6*.00
MEAN	53.24
MEDIAN	50.00
SKEWNESS	1.11
RANGE	2*2.00
VARIANCE	1745.35
STANDARD DEVIATION	41.87
95% CONF. (UPPER LIM.)	105.55
INTERVAL (LOWER LIM.)	-7*.50
COEF. OF VAR. (AS A %)	10*.41
ACCURACY (% REL. ERR.)	-1.17

MIDPOINT FREQ. HISTOGRAM

-33.200	1	X
26.400	15	XXXXXXXXXXXXXX
86.000	7	XXXXXXX
145.600	1	X
205.200	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-33.00	
.00	
2.00	
5.00	
13.00	
26.00	
30.00	
32.00	
33.00	
40.00	
40.00	
45.00	
55.00	
56.00	
58.00	
58.00	
72.00	
83.00	
74.00	
80.00	
82.00	
136.00	
165.00	
232.00	
235.00	

TABLE 23

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-BARBITURIC ACID METHOD
HIGH CONCENTRATION PAIR

A) AMPUL 2

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	30
INCREMENT	149.00
MEAN	176.93
MEDIAN	169.00
SKEWNESS	.66
RANGE	367.00
VARIANCE	5524.62
STANDARD DEVIATION	74.33
95% CONF. (UPPER LIM.)	204.95
INTERVAL (LOWER LIM.)	148.92
COEF. OF VAR. (AS A %)	42.01
ACCURACY (% REL. ERR.)	15.75

MIDPOINT FREQ. HISTOGRAM

82.700	7	XXXXXXX
152.100	11	XXXXXXXXXXX
221.500	10	XXXXXXXXXX
290.900	1	X
360.300	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

45.00	231.00
61.00	248.00
76.00	250.00
86.00	315.00
110.00	345.00
113.00	
117.00	
125.00	
128.00	
143.00	
149.00	
160.00	
166.00	
166.00	
167.00	
171.00	
184.00	
186.00	
204.00	
206.00	
210.00	
215.00	
220.00	
227.00	
228.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	24
INCREMENT	149.00
MEAN	198.46
MEDIAN	170.00
SKEWNESS	.96
RANGE	430.00
VARIANCE	13760.17
STANDARD DEVIATION	117.30
95% CONF. (UPPER LIM.)	246.45
INTERVAL (LOWER LIM.)	150.47
COEF. OF VAR. (AS A %)	59.14
ACCURACY (% REL. ERR.)	22.40

MIDPOINT FREQ. HISTOGRAM

51.200	7	XXXXXXX
199.600	8	XXXXXXXX
348.000	6	XXXXXX
496.400	1	X
	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

17.00	
35.00	
51.00	
77.00	
81.00	
95.00	
97.00	
130.00	
140.00	
141.00	
145.00	
170.00	
170.00	
185.00	
200.00	
211.00	
220.00	
220.00	
230.00	
235.00	
274.00	
340.00	
420.00	
504.00	

B) AMPUL 6

DISTILLED WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	30
INCREMENT	141.00
MEAN	164.60
MEDIAN	160.00
SKEWNESS	.59
RANGE	312.00
VARIANCE	4041.83
STANDARD DEVIATION	63.89
95% CONF. (UPPER LIM.)	295.27
INTERVAL (LOWER LIM.)	33.93
COEF. OF VAR. (AS A %)	38.81
ACCURACY (% REL. ERR.)	16.74

MIDPOINT FREQ. HISTOGRAM

51.200	1	X
113.600	11	XXXXXXXXXXX
176.000	13	XXXXXXXXXXXXX
238.400	2	XX
300.800	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

20.00	210.00
99.00	236.00
99.00	288.00
104.00	290.00
104.00	332.00
107.00	
115.00	
130.00	
133.00	
134.00	
135.00	
140.00	
147.00	
148.00	
160.00	
160.00	
170.00	
171.00	
171.00	
175.00	
180.00	
187.00	
189.00	
200.00	
204.00	

NATURAL WATER

STATISTICS: BASIC UNITS = UG/L

NUMBER OF VALUES RET.	24
INCREMENT	141.00
MEAN	152.00
MEDIAN	132.50
SKEWNESS	.85
RANGE	341.00
VARIANCE	7706.95
STANDARD DEVIATION	87.79
95% CONF. (UPPER LIM.)	343.41
INTERVAL (LOWER LIM.)	-39.41
COEF. OF VAR. (AS A %)	57.76
ACCURACY (% REL. ERR.)	7.80

MIDPOINT FREQ. HISTOGRAM

54.100	6	XXXXXX
130.300	10	XXXXXXXXXX
206.500	5	XXXXX
282.700	2	XX
358.900	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

15.00	
30.00	
45.00	
74.00	
81.00	
82.00	
104.00	
120.00	
121.00	
123.00	
127.00	
130.00	
135.00	
150.00	
154.00	
160.00	
160.00	
165.00	
165.00	
217.00	
225.00	
274.00	
300.00	
347.00	

TABLE 24

Statistical Summary

Cyanide Amenable to Chlorination

by

Pyridine-Barbituric Acid Method

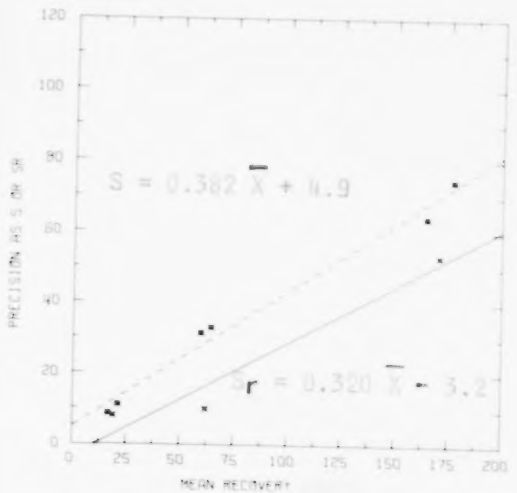
Statistical Parameters	Dist. Water Ampul 1	Dist. Water Ampul 3	Natrl. Water Ampul 1	Natrl. Water Ampul 3	Dist. Water Ampul 4	Dist. Water Ampul 5	Natrl. Water Ampul 4	Natrl. Water Ampul 5	Dist. Water Ampul 6	Dist. Water Ampul 2	Natrl. Water Ampul 6	Natrl. Water Ampul 2
True Value µg/L	13	18	13	18	64	64	64	64	141	149	141	149
Values Retained	27	28	24	24	28	28	21	25	30	30	24	24
Mean Recovery, µg/L ($\bar{X}$)	17	21	10	25	64	60	41	63	165	177	152	182
Accuracy as % Rel. Error	29	18	-25	41	0	-7	-35	-1	17	19	8	22
Std. Dev., µg/L (S)	9	11	13	31	33	31	31	69	64	74	88	117
Rel. Dev., %	51	52	135	122	51	52	75	109	39	42	58	64
Single-analyst Std. Dev., µg/L (S_r)	8		10		10		25		53		56	
Single-analyst Rel. Dev., %	39		131		16		47		31		33	

FIGURE 7

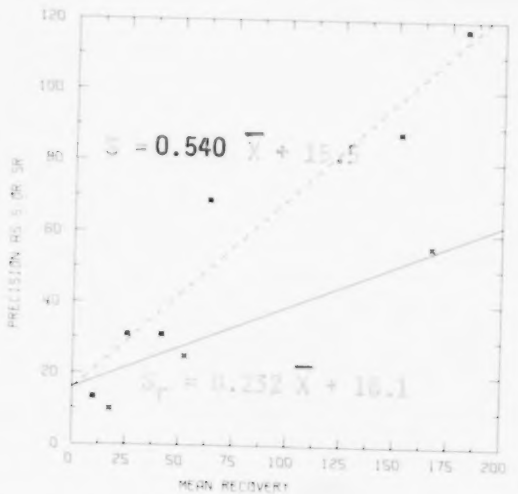
REGRESSION RESULTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-BARBITURIC ACID METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

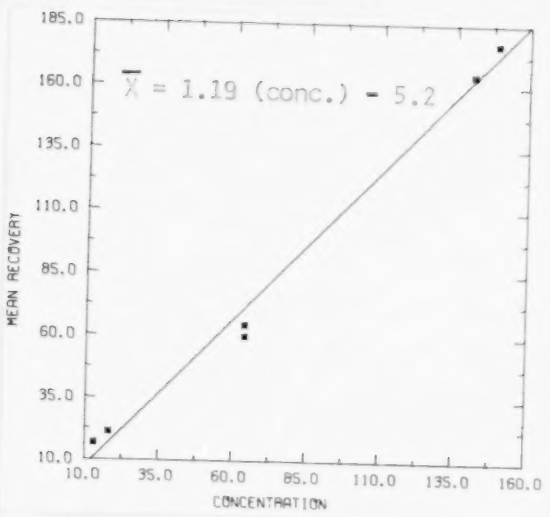


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

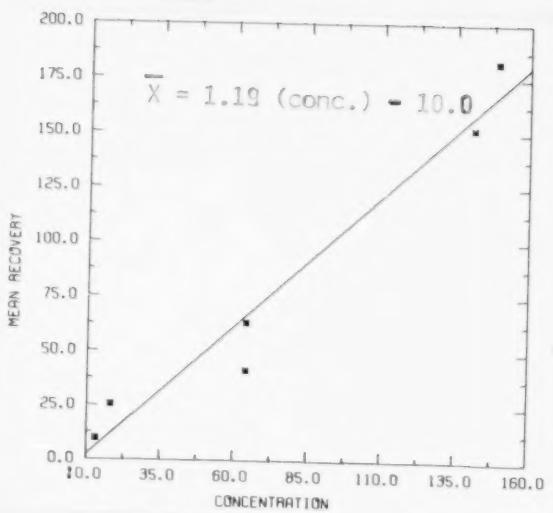
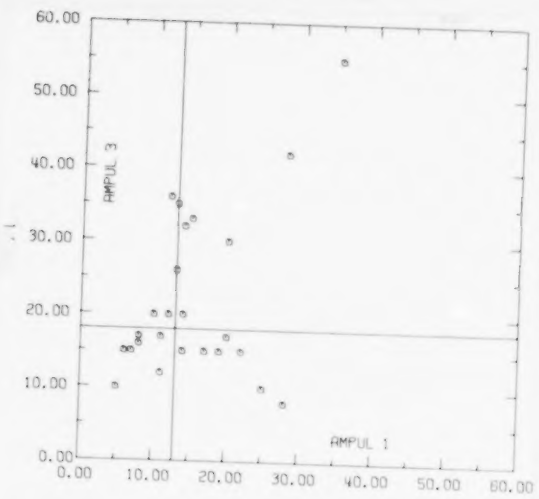


FIGURE 8

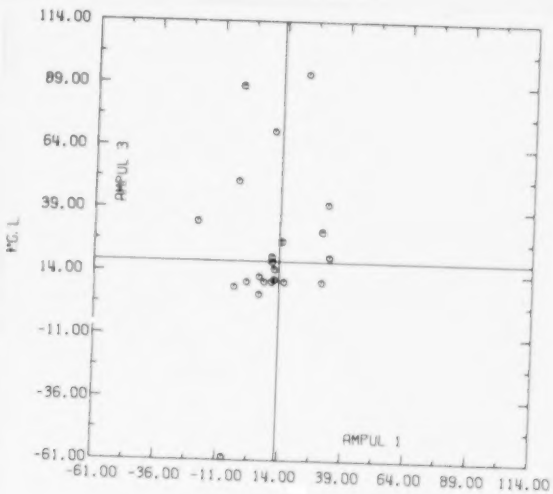
YOUDEN PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-BARBITURIC ACID METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

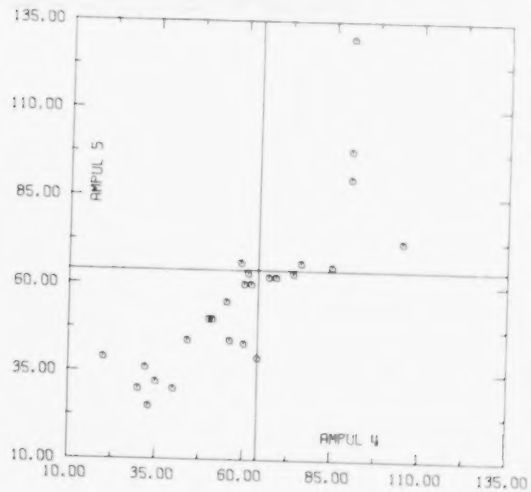


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

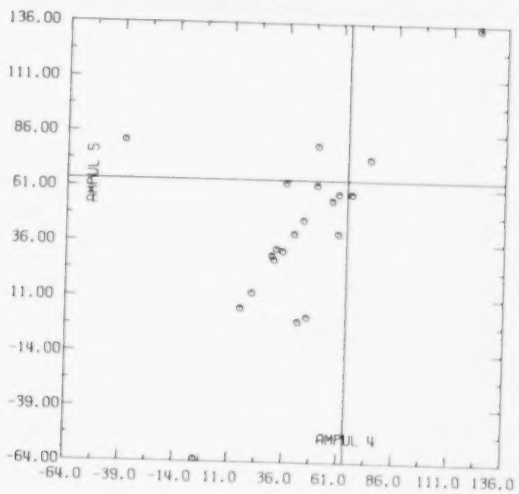
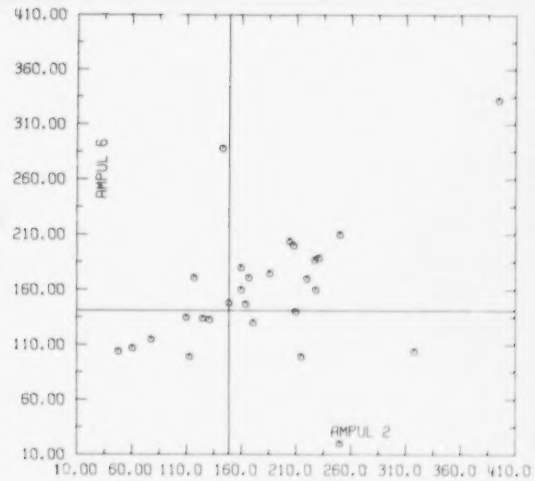


FIGURE 8
(continued)

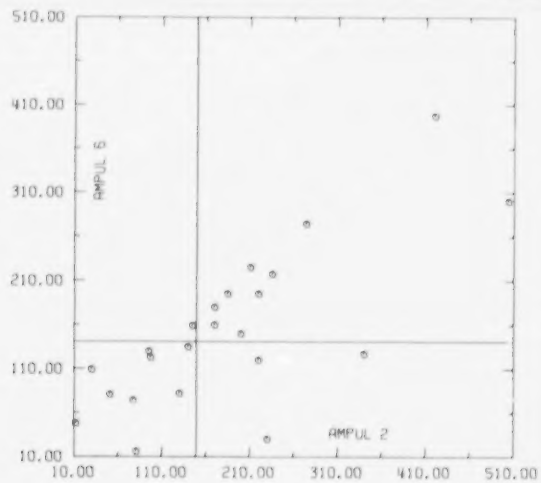
YOUDEN PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-BARBITURIC ACID METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



CATC, Pyridine-Pyrazolone Method

Tables 25 and 26 report distilled water data and natural water data from twelve and ten laboratories respectively. Data from one laboratory were rejected because the required procedure was not followed. Natural water data from two laboratories were rejected because the background levels were reported as "less than" values. Of particular note is the very limited data for Ampul 1 in natural water, which remains as a basis for statistical analysis.

The statistics and histograms in Tables 27, 28 and 29 show the effects of a few persistent outliers and a lack of strong centrality in the data. Symptomatic of such problems are the high coefficients of variation common to all levels in both water types.

The statistical summary in Table 30 also indicates serious problems. For example, the relative error statistics are generally quite high (over 20 percent) for the low level in distilled water and all levels in natural waters. In addition, the single analyst relative deviations for both waters actually increased as the concentration levels increased. Although there is limited data, such statistics are quite unusual and indicate generally poor performance in both types of water.

The Youden plot for the high concentration pairs in distilled water (Figure 10) is of special interest. From this plot it is obvious that the single analyst relative deviation of 46 percent in Table 30 was not caused by results from a single source, but was characteristic of most of the reported data. The resulting high estimate of S_r, relative to the estimate of S, caused the unusual crossover of the regression lines seen in Figure 9A for distilled water. The systematic error did not dominate here as it did in the other Youden plots.

TABLE 25

Raw Data for Cyanide Amenable to Chlorination

Pyridine-Pyrazolone Method

Recovery of Increment from Distilled Water

	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Increment In µg/L	13.00	149.00	18.00	64.00	64.00	141.00
Lab Code						
101	28.00	25.00	25.00	52.00	53.00	210.00
111		170.00	21.00	5.00	<5.00*	115.00
124	14.00	220.00	15.00	40.00	44.00	200.00
142	10.00	250.00	10.00	60.00	70.00	100.00
190		100.00	20.00	66.00	82.00	140.00
243					60.00	92.00
292	20.00	80.00	30.00	60.00	30.00	260.00
625	14.00	245.00	17.00	86.00	86.00	275.00
628		178.00	<5.00*	37.00	45.00	187.00
638	30.00	345.00	36.00	128.00	107.00	520.00*
650	188.00*IM	159.00*IM	94.00*IM	91.00*IM	91.00*IM	1.00*IM
651		185.00		40.00	50.00	100.00

* = Rejected
IM = Improper Method

TABLE 26

Raw Data for Cyanide Amenable to Chlorination

Pyridine-Pyrazolone Method

Recovery of Increment from Natural or Effluent Water

Increment In µg/L	Ampul 1 13.00	Ampul 2 149.00	Ampul 3 18.00	Ampul 4 64.00	Ampul 5 64.00	Ampul 6 141.00
Lab Code						
101	<25.00*	<32.00*	<24.00*	<53.00*	<40.00*	<180.00*
111		150.00	20.00	37.00	22.00	130.00
124	7.00	222.00	11.00	38.00	36.00	212.00
190		85.00	25.00	68.00	83.00	140.00
243		0.00				
292	<20.00*	<210.00*	<20.00*	<60.00*	<70.00*	<190.00*
625	5.00	145.00	6.00	62.00	70.00	130.00
628		352.00	180.00*	260.00	510.00*	380.00
638	28.00*	375.00	35.00	130.00	110.00	530.00
650	77.00*IM	212.00*IM	9.00*IM	0.00*IM	-90.00*IM	-91.00*IM

* = Rejected
IM = Improper Method

TABLE 27

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-PYRAZOLONE METHOD

LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	6	15.000	3	XXX
INCREMENT	13.00	25.000	3	XXX
MEAN	19.33			
MEDIAN	17.00			
SKEWNESS	.23			
RANGE	20.00			
VARIANCE	66.67			
STANDARD DEVIATION	8.16			
95% CONF. (UPPER LIM.)	40.32			
INTERVAL (LOWER LIM.)	-1.66			
COEF. OF VAR. (AS A %)	42.23			
ACCURACY (% REL. ERR.)	48.72			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

10.00
14.00
14.00
20.00
28.00
30.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	2	6.000	2	XX
INCREMENT	13.00			
MEAN	6.00			
MEDIAN	6.00			
SKEWNESS	.00			
RANGE	2.00			
VARIANCE	2.00			
STANDARD DEVIATION	1.41			
95% CONF. (UPPER LIM.)	23.97			
INTERVAL (LOWER LIM.)	-11.97			
COEF. OF VAR. (AS A %)	23.57			
ACCURACY (% REL. ERR.)	-53.85			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

5.00
7.00

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	8	14.333	3	XXX
INCREMENT	15.00	23.000	3	XXX
MEAN	21.75	31.667	2	XX
MEDIAN	20.50			
SKEWNESS	.31			
RANGE	26.00			
VARIANCE	70.21			
STANDARD DEVIATION	8.38			
95% CONF. (UPPER LIM.)	41.56			
INTERVAL (LOWER LIM.)	1.94			
COEF. OF VAR. (AS A %)	38.53			
ACCURACY (% REL. ERR.)	20.83			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

10.00
15.00
17.00
20.00
21.00
25.00
30.00
36.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	5	13.250	3	XXX
INCREMENT	15.00	27.750	2	XX
MEAN	19.40			
MEDIAN	20.00			
SKEWNESS	.13			
RANGE	24.00			
VARIANCE	131.30			
STANDARD DEVIATION	11.45			
95% CONF. (UPPER LIM.)	51.21			
INTERVAL (LOWER LIM.)	-12.41			
COEF. OF VAR. (AS A %)	59.07			
ACCURACY (% REL. ERR.)	7.74			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

6.00
11.00
20.00
25.00
35.00

TABLE 28

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION PYRIDINE -PYRAZOLONE METHOD

MEDIUM CONCENTRATION PAIR

AMPUL 4

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	10
INCREMENT	64.00
MEAN	57.40
MEDIAN	56.00
SKEWNESS	.60
RANGE	123.00
VARIANCE	1076.27
STANDARD DEVIATION	32.81
95% CONF. (UPPER LIM.)	131.61
INTERVAL (LOWER LIM.)	-16.81
COEF. OF VAR. (AS A %)	57.15
ACCURACY (% REL. ERR.)	-10.31

MIDPOINT	FREQ.	HISTOGRAM
25.500	4	XXXX
66.500	5	XXXXX
107.500	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

5.00
37.00
40.00
40.00
52.00
60.00
60.00
65.00
88.00
128.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	64.00
MEAN	99.17
MEDIAN	65.00
SKEWNESS	.96
RANGE	223.00
VARIANCE	7355.37
STANDARD DEVIATION	85.76
95% CONF. (UPPER LIM.)	314.63
INTERVAL (LOWER LIM.)	-121.30
COEF. OF VAR. (AS A %)	86.48
ACCURACY (% REL. ERR.)	54.95

MIDPOINT	FREQ.	HISTOGRAM
92.750	5	XXXXX
204.250	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

37.00
38.00
62.00
88.00
130.00
260.00

AMPUL 5

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	10
INCREMENT	64.00
MEAN	62.70
MEDIAN	56.50
SKEWNESS	.45
RANGE	77.00
VARIANCE	547.34
STANDARD DEVIATION	23.40
95% CONF. (UPPER LIM.)	115.63
INTERVAL (LOWER LIM.)	9.77
COEF. OF VAR. (AS A %)	37.31
ACCURACY (% REL. ERR.)	-2.03

MIDPOINT	FREQ.	HISTOGRAM
42.833	5	XXXXX
88.500	2	XX
94.167	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

30.00
44.00
45.00
50.00
54.00
60.00
70.00
82.00
88.00
107.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	5
INCREMENT	64.00
MEAN	64.20
MEDIAN	70.00
SKEWNESS	.02
RANGE	88.00
VARIANCE	1265.20
STANDARD DEVIATION	35.57
95% CONF. (UPPER LIM.)	162.96
INTERVAL (LOWER LIM.)	-34.56
COEF. OF VAR. (AS A %)	55.40
ACCURACY (% REL. ERR.)	.31

MIDPOINT	FREQ.	HISTOGRAM
44.000	2	XX
88.000	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

22.00
36.00
70.00
83.00
110.00

TABLE 29

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION PYRIDINE-PYRAZOLONE METHOD

HIGH CONCENTRATION PAIR

AMPUL 2

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	10
INCREMENT	149.00
MEAN	179.80
MEDIAN	181.50
SKEWNESS	-.00
RANGE	320.00
VARIANCE	8722.62
STANDARD DEVIATION	93.39
95% CONF. (UPPER LIM.)	391.08
INTERVAL (LOWER LIM.)	-31.48
COEF. OF VAR. (AS A %)	51.94
ACCURACY (% REL. ERR.)	20.67

MIDPOINT	FREQ.	HISTOGRAM
78.333	3	XXX
145.000	4	XXXX
291.667	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

25.00
80.00
100.00
170.00
178.00
185.00
220.00
245.00
250.00
345.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	149.00
MEAN	149.86
MEDIAN	150.00
SKEWNESS	.14
RANGE	375.00
VARIANCE	18707.14
STANDARD DEVIATION	136.77
95% CONF. (UPPER LIM.)	529.53
INTERVAL (LOWER LIM.)	-144.82
COEF. OF VAR. (AS A %)	72.04
ACCURACY (% REL. ERR.)	27.42

MIDPOINT	FREQ.	HISTOGRAM
62.500	2	XX
187.500	3	XXX
312.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

.00
85.00
145.00
150.00
222.00
352.00
375.00

AMPUL 6

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	10
INCREMENT	141.00
MEAN	167.90
MEDIAN	163.50
SKEWNESS	.28
RANGE	183.00
VARIANCE	4630.99
STANDARD DEVIATION	68.05
95% CONF. (UPPER LIM.)	321.65
INTERVAL (LOWER LIM.)	13.95
COEF. OF VAR. (AS A %)	40.53
ACCURACY (% REL. ERR.)	19.04

MIDPOINT	FREQ.	HISTOGRAM
122.500	5	XXXXX
183.500	3	XXX
244.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

92.00
100.00
100.00
115.00
140.00
187.00
200.00
210.00
260.00
275.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	141.00
MEAN	253.67
MEDIAN	176.00
SKEWNESS	.65
RANGE	400.00
VARIANCE	27512.67
STANDARD DEVIATION	165.87
95% CONF. (UPPER LIM.)	680.05
INTERVAL (LOWER LIM.)	-172.72
COEF. OF VAR. (AS A %)	65.39
ACCURACY (% REL. ERR.)	79.91

MIDPOINT	FREQ.	HISTOGRAM
230.000	4	XXXX
430.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

130.00
130.00
140.00
212.00
380.00
530.00

TABLE 30

Statistical Summary

Cyanide Amenable to Chlorination

by

Pyridine-Pyrazolone Method

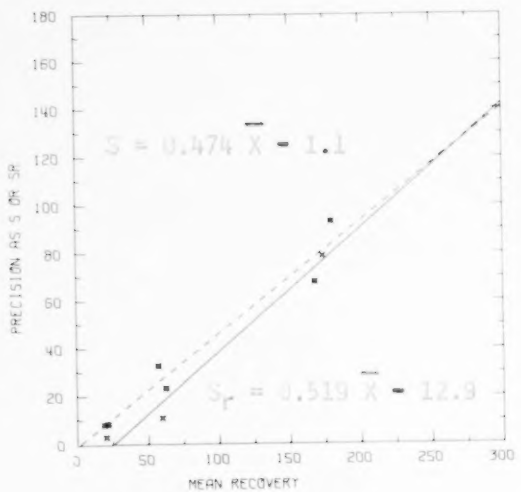
Statistical Parameters	Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul	
	1	3	1	3	4	5	4	5	6	2	6	2
True Value, µg/L	13	18	13	18	64	64	64	64	141	149	141	149
Values Retained	6	8	2	5	10	10	6	5	10	10	6	7
Mean Recovery, µg/L ($\bar{X}$)	19	22	6	19	57	63	99	64	168	180	254	190
Accuracy as % Rel. Error	49	21	-54	8	-10	-2	55	0	19	21	80	27
Std. Dev., µg/L (S)	8	8	1	11	33	23	86	36	68	93	166	137
Rel. Dev., %	42	39	24	59	57	37	86	55	41	52	65	72
Range, µg/L	20	26	2	29	123	77	223	88	183	320	400	375
Single Analyst Std. Dev., µg/L (S_r)	3		2		11		11		79		47	
Single Analyst Rel. Dev., %	16		12		18		13		46		21	

FIGURE 9

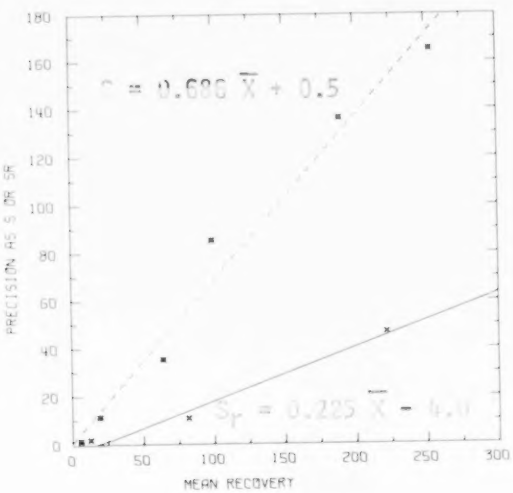
REGRESSION RESULTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-PYRAZOLONE METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

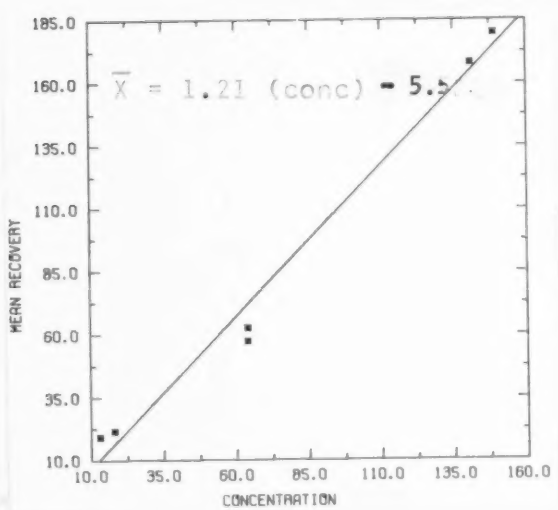


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

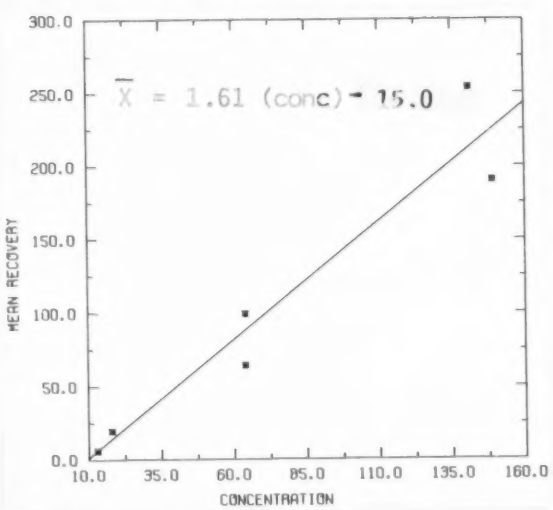
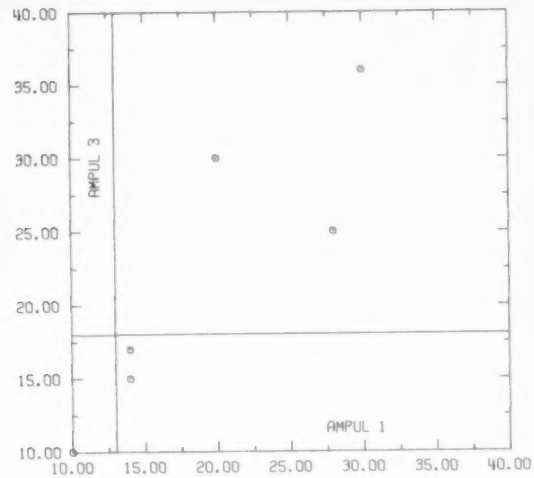


FIGURE 10

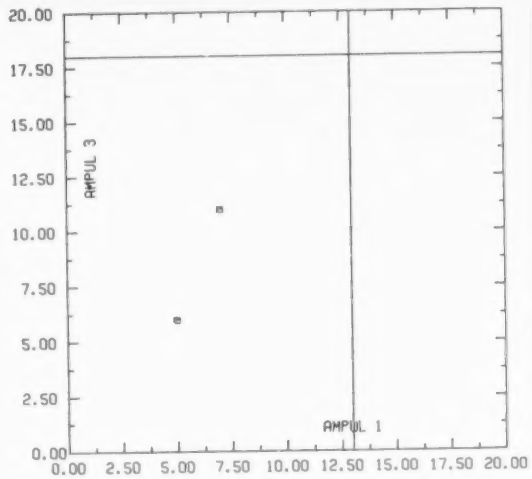
YOUDEN PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-PYRAZOLONE METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

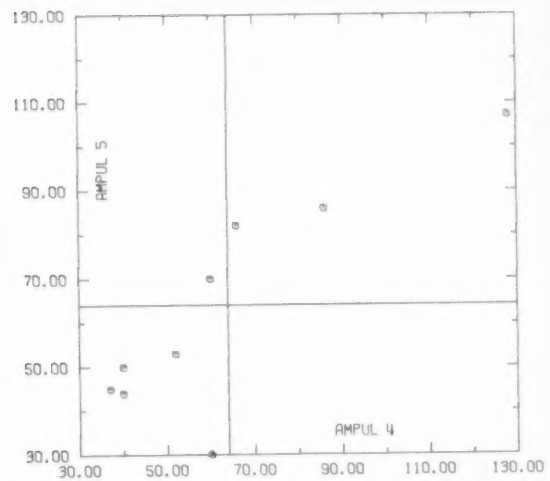


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

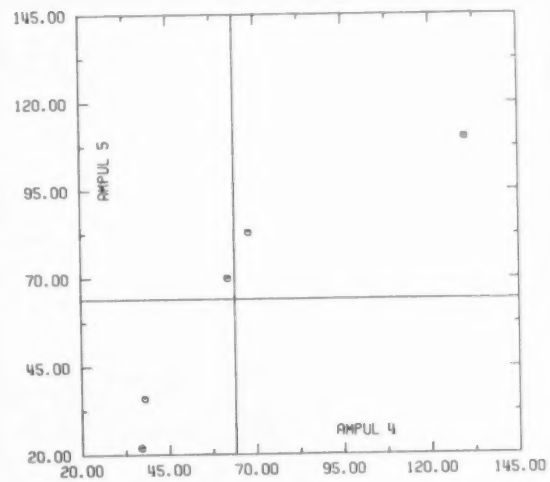
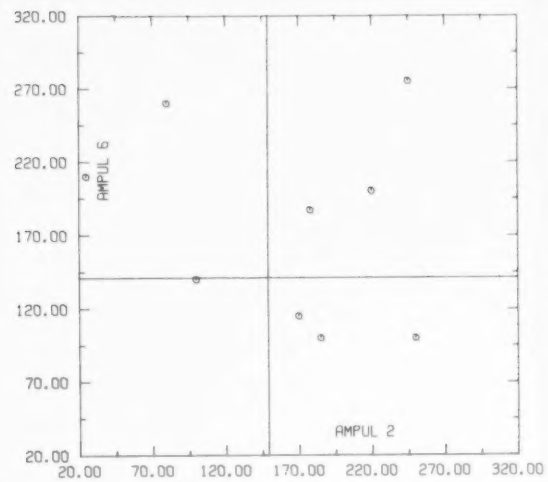


FIGURE 10
(continued)

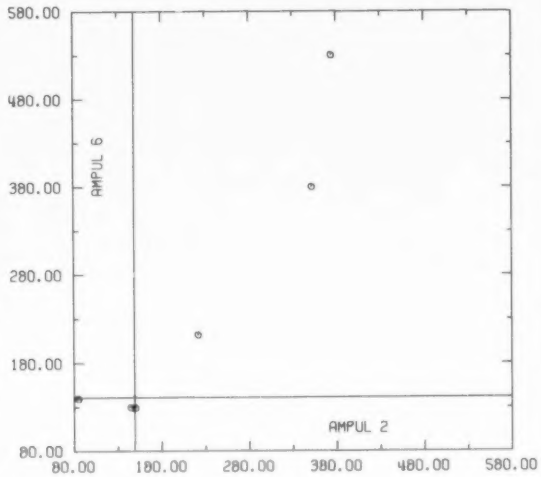
YOUDON PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
PYRIDINE-PYRAZOLONE METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



CATC, Electrode Method

Eight laboratories reported distilled water data and seven reported natural water data in Tables 31 and 32. The natural water data from one laboratory were rejected because the background level was reported as a "less than" value.

The histograms in Tables 33 through 35 indicate poor centrality as before, but unlike the earlier methods there is broad dispersion of results rather than a few values which stand out as outliers.

Summary Table 36 indicates a high bias at all levels and in all waters, although the bias appears somewhat smaller for natural waters. This apparent advantage in natural waters is offset by the relative deviations, which are high at all levels for both waters, but are highest for the natural waters. The precision and accuracy plots in Figure 11 depict and support the statistics and conclusions drawn from Table 36.

The Youden plots in Figure 12 show that the reported data were widely distributed and with no obvious outliers to explain the large deviations and relative errors in Table 36.

TABLE 31

Raw Data for Cyanide Amenable to Chlorination

Electrode Method

Recovery of Increment from Distilled Water

	Ampul 1	Ampul 2	Ampul 3	Ampul 4	Ampul 5	Ampul 6
Increment In µg/L	13.00	149.00	18.00	64.00	64.00	141.00
Lab Code						
292	40.00	220.00	0.00	140.00	580.00*	390.00
438	11.00	135.00	28.00	62.00	64.00	125.00
624	40.00	600.00	70.00	100.00	100.00	500.00
627	26.00	484.00	37.00	170.00	152.00	290.00
631	7.00	130.00	2.00	43.00	54.00	116.00
635			13.00	51.00	45.00	43.00
638	30.00	345.00	36.00	128.00	107.00	520.00
642	4.00	0.00	6.00	100.00	86.00	100.00

* = Rejected

TABLE 32

Raw Data for Cyanide Amenable to Chlorination

Electrode Method

Recovery of Increment from Natural or Effluent Water

Increment In µg/L	Ampul 1 13.00	Ampul 2 149.00	Ampul 3 18.00	Ampul 4 64.00	Ampul 5 64.00	Ampul 6 141.00
Lab Code						
292	<20.00*	<330.00*	<30.00*	<100.00*	<110.00*	<220.00*
438	-73.00	139.00	24.00	59.00	31.00	179.00
627		434.00	33.00	165.00	170.00	295.00
631	138.00	80.00	1046.00*	-75.00	44.00	-40.00
635			5.00	-13.00	15.00	86.00
638	28.00	375.00	35.00	130.00	110.00	530.00
642	-12.00	-24.00	26.00	-20.00	25.00	52.00

* = Rejected

TABLE 33

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION ELECTRODE METHOD

LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	13.00
MEAN	22.57
MEDIAN	26.00
SKEWNESS	-.03
RANGE	36.00
VARIANCE	232.62
STANDARD DEVIATION	15.25
95% CONF. (UPPER LIM.)	59.84
INTERVAL (LOWER LIM.)	-14.75
COEF. OF VAR. (AS A %)	67.57
ACCURACY (% REL. ERR.)	73.63

MIDPOINT	FREQ.	HISTOGRAM
10.000	3	XXX
22.000	1	X
34.000	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

4.00
7.00
11.00
26.00
30.00
40.00
40.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	4
INCREMENT	13.00
MEAN	20.25
MEDIAN	8.00
SKEWNESS	.28
RANGE	211.00
VARIANCE	7886.92
STANDARD DEVIATION	88.81
95% CONF. (UPPER LIM.)	302.88
INTERVAL (LOWER LIM.)	-262.38
COEF. OF VAR. (AS A %)	438.56
ACCURACY (% REL. ERR.)	55.77

MIDPOINT	FREQ.	HISTOGRAM
-20.250	3	XXX
85.250	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-73.00
-12.00
28.00
138.00

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	14.00
MEAN	24.00
MEDIAN	20.50
SKEWNESS	.65
RANGE	70.00
VARIANCE	564.29
STANDARD DEVIATION	23.75
95% CONF. (UPPER LIM.)	80.17
INTERVAL (LOWER LIM.)	-32.17
COEF. OF VAR. (AS A %)	98.98
ACCURACY (% REL. ERR.)	33.33

MIDPOINT	FREQ.	HISTOGRAM
11.667	4	XXXX
35.000	3	XXX
58.333	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

.00
2.00
5.00
13.00
28.00
36.00
37.00
70.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	5
INCREMENT	15.00
MEAN	24.60
MEDIAN	25.00
SKEWNESS	-.69
RANGE	30.00
VARIANCE	141.30
STANDARD DEVIATION	11.89
95% CONF. (UPPER LIM.)	57.60
INTERVAL (LOWER LIM.)	-8.40
COEF. OF VAR. (AS A %)	48.32
ACCURACY (% REL. ERR.)	36.67

MIDPOINT	FREQ.	HISTOGRAM
12.500	1	X
27.500	4	XXXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

5.00
24.00
26.00
33.00
35.00

TABLE 34

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION ELECTRODE METHOD

MEDIUM CONCENTRATION PAIR

AMPUL 4

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	64.00
MEAN	99.25
MEDIAN	100.00
SKEWNESS	.14
RANGE	127.00
VARIANCE	2053.36
STANDARD DEVIATION	45.31
95% CONF. (UPPER LIM.)	206.40
INTERVAL (LOWER LIM.)	-7.90
COEF. OF VAR. (AS A %)	45.66
ACCURACY (% REL. ERR.)	55.08

MIDPOINT	FREQ.	HISTOGRAM
64.167	3	XXX
106.500	2	XX
148.833	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

43.00	
51.00	
62.00	
100.00	
100.00	
128.00	
140.00	
170.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	64.00
MEAN	41.00
MEDIAN	23.00
SKEWNESS	.14
RANGE	240.00
VARIANCE	8742.80
STANDARD DEVIATION	93.50
95% CONF. (UPPER LIM.)	281.36
INTERVAL (LOWER LIM.)	-199.36
COEF. OF VAR. (AS A %)	228.06
ACCURACY (% REL. ERR.)	-35.94

MIDPOINT	FREQ.	HISTOGRAM
-15.000	3	XXX
105.000	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-75.00
-20.00
-13.00
59.00
130.00
165.00

AMPUL 5

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	64.00
MEAN	86.86
MEDIAN	88.00
SKEWNESS	.47
RANGE	107.00
VARIANCE	1362.81
STANDARD DEVIATION	36.92
95% CONF. (UPPER LIM.)	177.19
INTERVAL (LOWER LIM.)	-3.47
COEF. OF VAR. (AS A %)	42.50
ACCURACY (% REL. ERR.)	35.71

MIDPOINT	FREQ.	HISTOGRAM
62.833	3	XXX
98.500	3	XXX
134.167	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

45.00	
54.00	
84.00	
88.00	
100.00	
107.00	
152.00	

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	64.00
MEAN	65.83
MEDIAN	37.50
SKEWNESS	.70
RANGE	155.00
VARIANCE	3748.57
STANDARD DEVIATION	61.23
95% CONF. (UPPER LIM.)	223.22
INTERVAL (LOWER LIM.)	-91.55
COEF. OF VAR. (AS A %)	93.00
ACCURACY (% REL. ERR.)	2.86

MIDPOINT	FREQ.	HISTOGRAM
53.750	4	XXXX
131.250	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

15.00
25.00
31.00
44.00
110.00
170.00

TABLE 35

DATA SUMMARIES FOR CYANIDE AMENABLE TO CHLORINATION ELECTRODE METHOD

HIGH CONCENTRATION PAIR

AMPUL 2

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	7
INCREMENT	149.00
MEAN	273.43
MEDIAN	220.00
SKEWNESS	.27
RANGE	600.00
VARIANCE	45577.29
STANDARD DEVIATION	213.49
95% CONF. (UPPER LIM.)	795.81
INTERVAL (LOWER LIM.)	-248.96
COEF. OF VAR. (AS A %)	78.08
ACCURACY (% REL. ERR.)	83.51

MIDPOINT	FREQ.	HISTOGRAM
100.000	3	XXX
300.000	2	XX
500.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

.00
130.00
135.00
220.00
345.00
484.00
600.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	5
INCREMENT	149.00
MEAN	200.80
MEDIAN	139.00
SKEWNESS	.12
RANGE	458.00
VARIANCE	38418.70
STANDARD DEVIATION	196.01
95% CONF. (UPPER LIM.)	744.99
INTERVAL (LOWER LIM.)	-343.39
COEF. OF VAR. (AS A %)	97.61
ACCURACY (% REL. ERR.)	34.77

MIDPOINT	FREQ.	HISTOGRAM
90.500	3	XXX
319.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-24.00
80.00
139.00
375.00
434.00

AMPUL 6

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	8
INCREMENT	141.00
MEAN	260.50
MEDIAN	207.50
SKEWNESS	.24
RANGE	477.00
VARIANCE	36378.29
STANDARD DEVIATION	190.73
95% CONF. (UPPER LIM.)	711.50
INTERVAL (LOWER LIM.)	-190.50
COEF. OF VAR. (AS A %)	73.22
ACCURACY (% REL. ERR.)	84.75

MIDPOINT	FREQ.	HISTOGRAM
122.500	4	XXXX
281.500	1	X
440.500	3	XXX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

43.00
100.00
116.00
125.00
290.00
390.00
500.00
520.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	6
INCREMENT	141.00
MEAN	183.67
MEDIAN	132.50
SKEWNESS	.56
RANGE	570.00
VARIANCE	41853.07
STANDARD DEVIATION	204.58
95% CONF. (UPPER LIM.)	709.56
INTERVAL (LOWER LIM.)	-342.23
COEF. OF VAR. (AS A %)	111.39
ACCURACY (% REL. ERR.)	30.26

MIDPOINT	FREQ.	HISTOGRAM
102.500	4	XXXX
387.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

-40.00
52.00
86.00
174.00
245.00
530.00

TABLE 36

Statistical Summary

Cyanide Amenable to Chlorination

by

Electrode Method

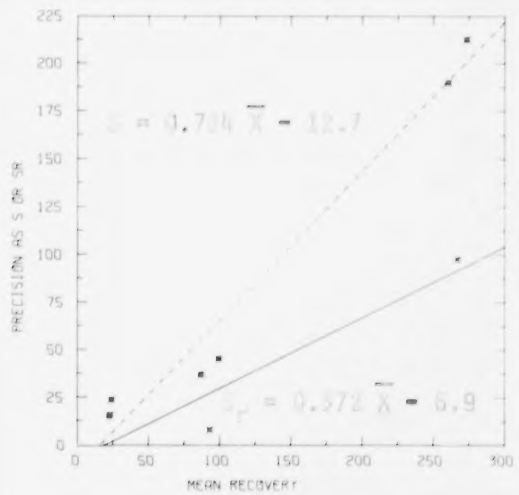
Statistical Parameters	Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul		Dist. Water Ampul		Natrl. Water Ampul	
	1	3	1	3	4	5	4	5	6	2	6	2
True Value µg/L	13	18	13	18	64	64	64	64	141	149	141	149
Values Retained	7	8	4	5	8	7	6	6	8	7	6	5
Mean Recovery, µg/L ($\bar{X}$)	23	24	20	25	99	87	41	66	261	273	184	201
Accuracy as % Rel. Error	74	33	56	37	55	36	-36	3	85	84	30	35
Std. Dev., µg/L (S)	15	24	89	12	45	37	93	61	191	213	205	196
Rel. Dev., %	68	99	439	48	46	43	228	93	73	78	111	98
Range, µg/L	36	70	211	30	127	107	240	155	477	600	570	458
Single Analyst Std. Dev., µg/L (S_r)	16		32		8		38		98		90	
Single Analyst Rel. Dev., %	66		144		9		72		37		47	

FIGURE 11

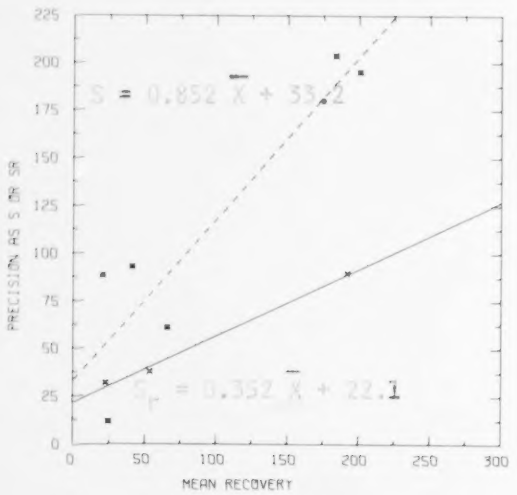
REGRESSION RESULTS FOR CYANIDE AMENABLE TO CHLORINATION
ELECTRODE METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

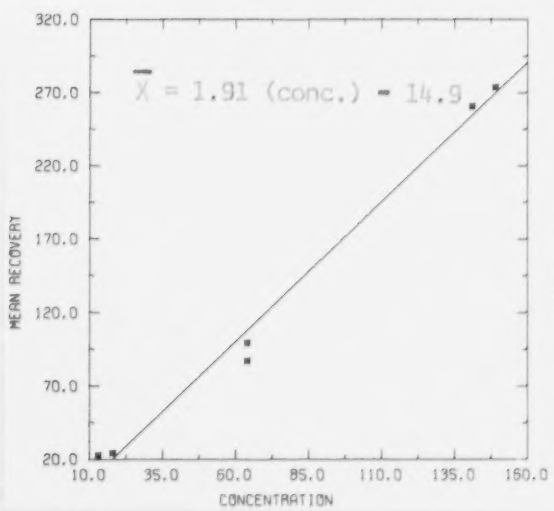


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

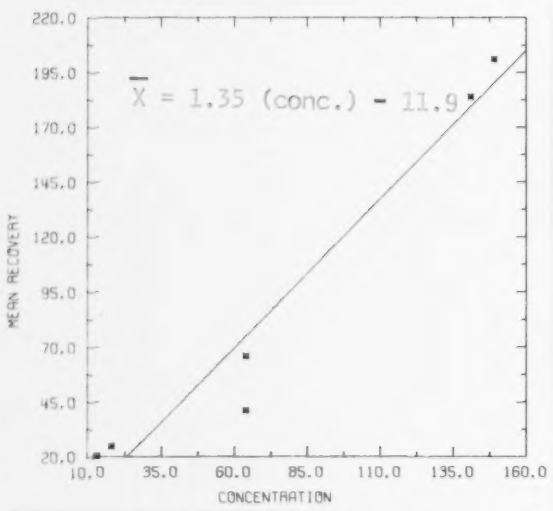
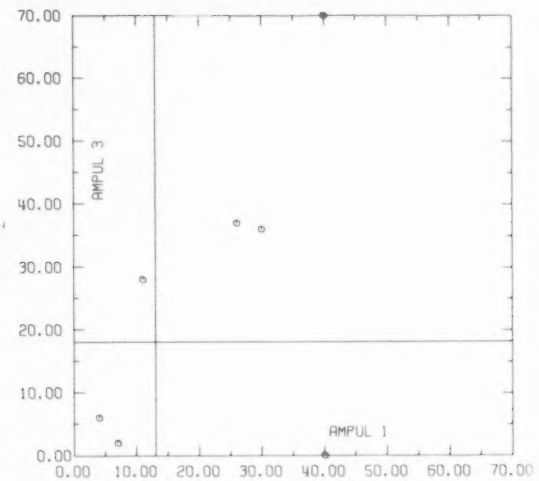


FIGURE 12

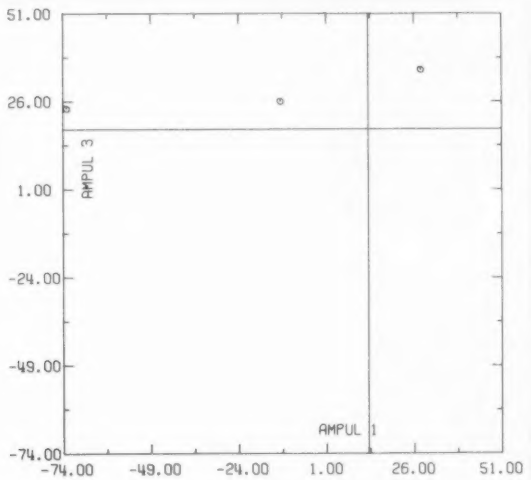
YOUDEN PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
ELECTRODE METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

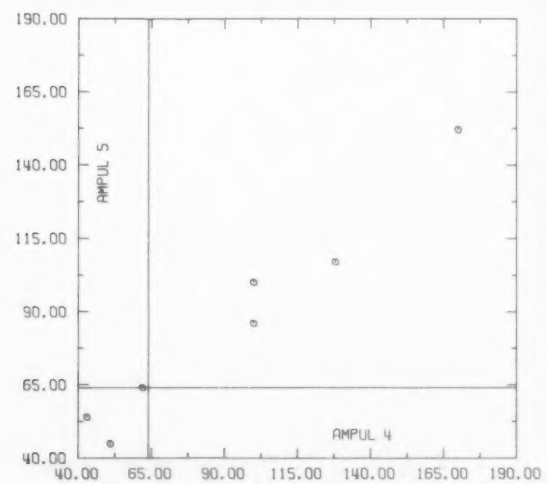


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

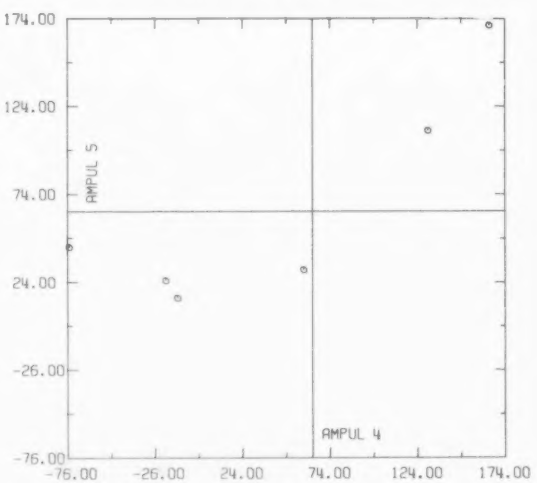
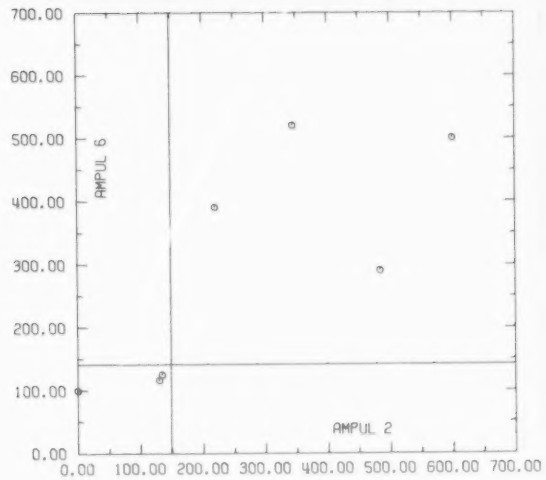


FIGURE 12
(continued)

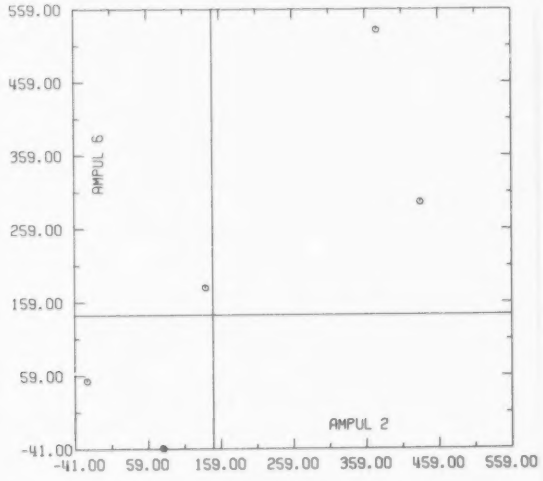
YOUDEN PLOTS FOR CYANIDE AMENABLE TO CHLORINATION
ELECTRODE METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



Summary for CATC in Natural Waters

The mean recovery ($\bar{X}$), overall standard deviation (S), and single analyst standard deviation (S_r) results for natural water analyses by each of the methods, within the concentration range 13-150 µg/liter, are as follows.

Method	$\bar{X}$	S	S_r
P-B*	1.19 (conc.) - 10.0	0.540 $\bar{X}$ + 15.5	0.232 $\bar{X}$ + 16.1
P-P**	1.61 (conc.) - 15.0	0.686 $\bar{X}$ - 0.5	0.225 $\bar{X}$ - 4.0
Electrode	1.35 (conc.) - 11.9	0.852 $\bar{X}$ + 33.2	0.352 $\bar{X}$ + 22.1

At the extremes of the applicable range, these equations lead to the following statistical estimated in µg/liter.

	At 13 µg/liter			At 150 µg/liter		
Method	$\bar{X}$	S	S_r	$\bar{X}$	S	S_r
P-B*	5.47	22.5	19.1	168.5	96.5	50.9
P-P**	5.93	9.4	-1.1[a]	226.5	103.4	29.8
Electrode	5.65	44.3	26.7	190.6	161.0	74.9

* Pyridine-barbituric acid
** Pyridine-pyrazolone

a The variance-estimating equations for this method are not valid at this low concentration.

Although these tables show slightly better statistics for the pyridine-barbituric acid method, the CATC statistics for all methods look very unsatisfactory. This suggests an inherent problem within the CATC definition rather than a problem with measurement technique applied.

Roberts-Jackson Method

The objective of the Roberts-Jackson method is the same as that of the CATC procedures; to isolate and measure free and easily decomplexed cyanides separately from all other cyanide complexes. In this method, the conventional Serfass distillation and colorimetric procedures are used, but the sample is only mildly acidified, in contrast to the intense acidification in the usual Serfass operation, and zinc acetate is substituted for cuprous chloride in the distillation procedure. The use of zinc acetate is intended to suppress decomposition of ferro-cyanide complexes that may be present in the sample. In theory, only the so-called free cyanides would be stripped from the sample and measured. The Roberts-Jackson method, therefore, should yield results very similar to the CATC procedures.

Despite the fact that a number of industrial laboratories requested this method be included in the study, only three participants used it. Consequently, data for the Roberts-Jackson method in Tables 37 through 42 and in Figures 13 and 14 are sparse and of very limited value. This is particularly unfortunate because the data submitted appeared more precise and accurate than the CATC data.

TABLE 37

Raw Data for Cyanide by the Roberts-Jackson Method

Recovery of Increment from Distilled Water

Increment In µg/L	Ampul 1 13.00	Ampul 2 149.00	Ampul 3 18.00	Ampul 4 64.00	Ampul 5 64.00	Ampul 6 141.00
Lab Code						
438		125.00	15.00	55.00		
628	12.00	133.00	20.00	49.00	55.00	121.00
639	16.00	153.00	22.00	70.00	63.00	157.00

TABLE 38

Raw Data for Cyanide by the Roberts-Jackson Method

Recovery of Increment from Natural or Effluent Water

Increment In µg/L	Ampul 1 13.00	Ampul 2 149.00	Ampul 3 18.00	Ampul 4 64.00	Ampul 5 64.00	Ampul 6 141.00
Lab Code						
628	28.00	140.00	27.00	64.00	65.00	123.00
639	14.00	145.00	18.00	58.00	52.00	129.00

TABLE 39

DATA SUMMARIES FOR CYANIDE BY THE ROBERTS-JACKSON METHOD

LOW CONCENTRATION PAIR

AMPUL 1

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	2	14.000	2	XX
INCREMENT	13.00			
MEAN	14.00			
MEDIAN	14.00			
SKEWNESS	.00			
RANGE	4.00			
VARIANCE	8.00			
STANDARD DEVIATION	2.83			
95% CONF. (UPPER LIM.)	49.94			
INTERVAL (LOWER LIM.)	-21.94			
COEF. OF VAR. (AS A %)	20.20			
ACCURACY (% REL. ERR.)	7.69			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

12.00
16.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	2	21.000	2	XX
INCREMENT	13.00			
MEAN	21.00			
MEDIAN	21.00			
SKEWNESS	.00			
RANGE	14.00			
VARIANCE	98.00			
STANDARD DEVIATION	9.90			
95% CONF. (UPPER LIM.)	146.78			
INTERVAL (LOWER LIM.)	-104.78			
COEF. OF VAR. (AS A %)	47.14			
ACCURACY (% REL. ERR.)	61.54			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

14.00
28.00

AMPUL 3

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	3	16.750	1	X
INCREMENT	18.00	20.250	2	XX
MEAN	19.00			
MEDIAN	20.00			
SKEWNESS	-.26			
RANGE	7.00			
VARIANCE	13.00			
STANDARD DEVIATION	3.61			
95% CONF. (UPPER LIM.)	34.51			
INTERVAL (LOWER LIM.)	3.49			
COEF. OF VAR. (AS A %)	18.98			
ACCURACY (% REL. ERR.)	5.56			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

15.00
20.00
22.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L	MIDPOINT	FREQ.	HISTOGRAM
NUMBER OF VALUES RET.	2	22.500	2	XX
INCREMENT	18.00			
MEAN	22.50			
MEDIAN	22.50			
SKEWNESS	.00			
RANGE	9.00			
VARIANCE	40.50			
STANDARD DEVIATION	6.36			
95% CONF. (UPPER LIM.)	103.36			
INTERVAL (LOWER LIM.)	-58.36			
COEF. OF VAR. (AS A %)	28.28			
ACCURACY (% REL. ERR.)	25.00			

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

18.00
27.00

TABLE 40

DATA SUMMARIES FOR CYANIDE BY THE ROBERTS-JACKSON METHOD

MEDIUM CONCENTRATION PAIR

AMPUL 4

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	3
INCREMENT	64.00
MEAN	58.00
MEDIAN	.00
SKEWNESS	.26
RANGE	21.00
VARIANCE	117.00
STANDARD DEVIATION	10.82
95% CONF. (UPPER LIM.)	104.54
INTERVAL (LOWER LIM.)	11.46
COEF. OF VAR. (AS A %)	18.65
ACCURACY (% REL. ERR.)	-9.38

MIDPOINT	FREQ.	HISTOGRAM
54.250	2	XX
64.750	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

49.00
55.00
70.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	64.00
MEAN	61.00
MEDIAN	61.00
SKEWNESS	.00
RANGE	6.00
VARIANCE	18.00
STANDARD DEVIATION	4.24
95% CONF. (UPPER LIM.)	114.91
INTERVAL (LOWER LIM.)	7.09
COEF. OF VAR. (AS A %)	6.96
ACCURACY (% REL. ERR.)	-4.69

MIDPOINT	FREQ.	HISTOGRAM
61.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

58.00
64.00

AMPUL 5

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	64.00
MEAN	59.00
MEDIAN	59.00
SKEWNESS	.00
RANGE	8.00
VARIANCE	32.00
STANDARD DEVIATION	5.66
95% CONF. (UPPER LIM.)	130.88
INTERVAL (LOWER LIM.)	-12.88
COEF. OF VAR. (AS A %)	9.59
ACCURACY (% REL. ERR.)	-7.81

MIDPOINT	FREQ.	HISTOGRAM
59.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

55.00
63.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	64.00
MEAN	58.50
MEDIAN	58.50
SKEWNESS	.00
RANGE	13.00
VARIANCE	84.50
STANDARD DEVIATION	9.19
95% CONF. (UPPER LIM.)	175.30
INTERVAL (LOWER LIM.)	-58.30
COEF. OF VAR. (AS A %)	15.71
ACCURACY (% REL. ERR.)	-8.54

MIDPOINT	FREQ.	HISTOGRAM
58.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

52.00
65.00

TABLE 41

DATA SUMMARIES FOR CYANIDE BY THE ROBERTS-JACKSON METHOD

HIGH CONCENTRATION PAIR

AMPUL 2

A) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	3
INCREMENT	149.00
MEAN	137.00
MEDIAN	133.00
SKEWNESS	.26
RANGE	28.00
VARIANCE	208.00
STANDARD DEVIATION	14.42
95% CONF. (UPPER LIM.)	199.05
INTERVAL (LOWER LIM.)	74.95
COEF. OF VAR. (AS A %)	10.53
ACCURACY (% REL. ERR.)	-8.05

MIDPOINT	FREQ.	HISTOGRAM
132.000	2	XX
146.000	1	X

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

125.00
133.00
153.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	149.00
MEAN	142.50
MEDIAN	142.50
SKEWNESS	.00
RANGE	5.00
VARIANCE	12.50
STANDARD DEVIATION	3.54
95% CONF. (UPPER LIM.)	187.42
INTERVAL (LOWER LIM.)	97.58
COEF. OF VAR. (AS A %)	2.48
ACCURACY (% REL. ERR.)	-4.36

MIDPOINT	FREQ.	HISTOGRAM
142.500	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

140.00
145.00

AMPUL 6

B) DISTILLED WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	141.00
MEAN	139.00
MEDIAN	139.00
SKEWNESS	.00
RANGE	36.00
VARIANCE	648.00
STANDARD DEVIATION	25.46
95% CONF. (UPPER LIM.)	462.84
INTERVAL (LOWER LIM.)	-184.84
COEF. OF VAR. (AS A %)	18.31
ACCURACY (% REL. ERR.)	-1.42

MIDPOINT	FREQ.	HISTOGRAM
139.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

121.00
157.00

NATURAL WATER

STATISTICS:	BASIC UNITS = UG/L
NUMBER OF VALUES RET.	2
INCREMENT	141.00
MEAN	126.00
MEDIAN	126.00
SKEWNESS	.00
RANGE	6.00
VARIANCE	18.00
STANDARD DEVIATION	4.24
95% CONF. (UPPER LIM.)	179.91
INTERVAL (LOWER LIM.)	72.09
COEF. OF VAR. (AS A %)	3.37
ACCURACY (% REL. ERR.)	-10.64

MIDPOINT	FREQ.	HISTOGRAM
126.000	2	XX

RETAINED DATA IN ASCENDING ORDER BY COLUMNS:

123.00
129.00

TABLE 42

Statistical Summary

Cyanide by the Roberts-Jackson Method

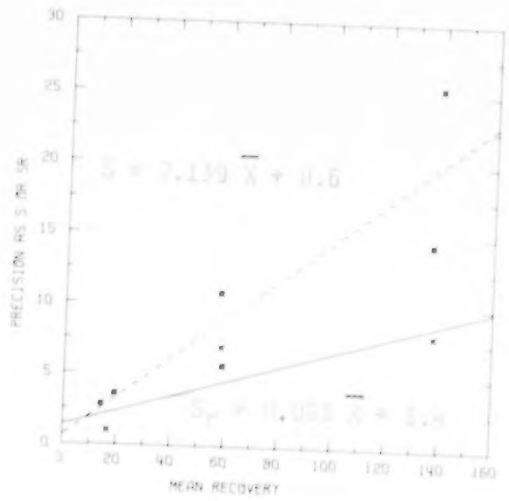
Statistical Parameters	Dist. Water Ampul 1	Dist. Water Ampul 3	Natrl. Water Ampul 1	Natrl. Water Ampul 3	Dist. Water Ampul 4	Dist. Water Ampul 5	Natrl. Water Ampul 4	Natrl. Water Ampul 5	Dist. Water Ampul 6	Dist. Water Ampul 2	Natrl. Water Ampul 6	Natrl. Water Ampul 2
True Value µg/L	13	18	13	18	64	64	64	64	141	149	141	149
Values Retained	2	3	2	2	3	2	2	2	2	3	2	2
Mean Recovery, µg/L ($\bar{X}$)	14	19	21	23	58	59	61	59	139	137	126	143
Accuracy as % Rel. Error	8	6	62	28	-9	-8	-5	-9	-1	-8	-11	-4
Std. Dev., µg/L (S)	3	4	10	6	11	6	4	9	25	14	4	4
Rel. Dev., %	20	19	47	28	19	10	7	16	18	11	3	2
Range, µg/L	4	7	14	9	21	8	6	13	36	28	6	5
Single Analyst Std. Dev., µg/L (S_r)	1		3		7		4		8		1	
Single Analyst Rel. Dev., %	6		12		11		6		6		1	

FIGURE 13

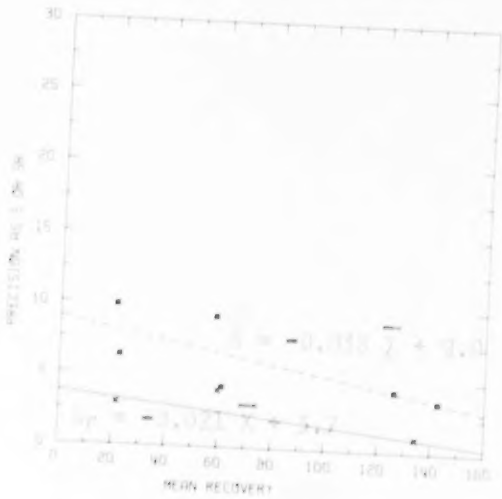
REGRESSION RESULTS FOR CYANIDE BY THE ROBERTS-JACKSON METHOD

PRECISION PLOTS IN UG/L

A) DISTILLED WATER

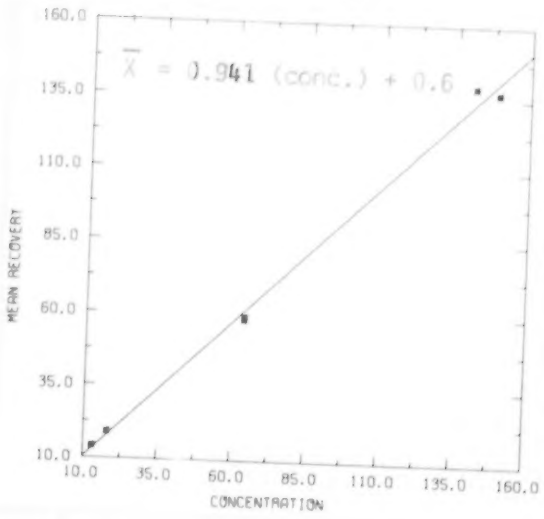


NATURAL WATER



ACCURACY PLOTS IN UG/L

B) DISTILLED WATER



NATURAL WATER

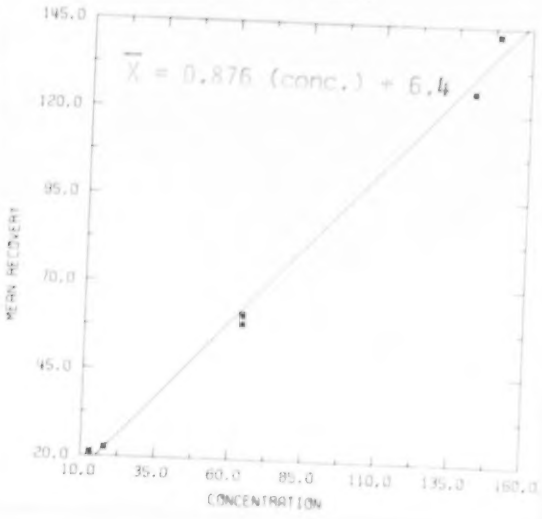
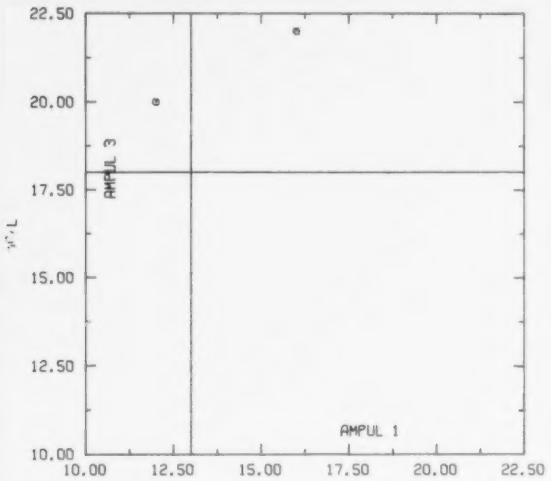


FIGURE 14

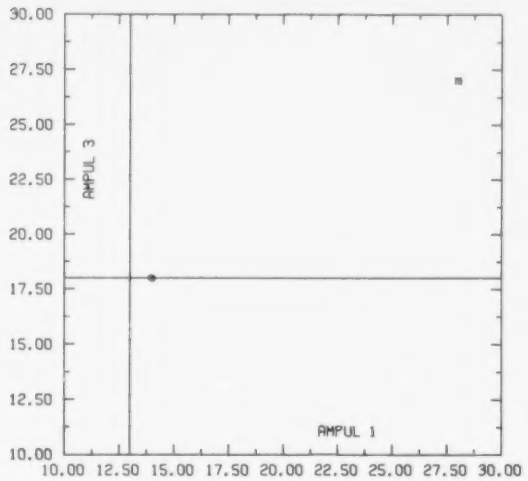
YOUDEN PLOTS FOR CYANIDE BY THE
ROBERTS-JACKSON METHOD

LOW CONCENTRATION PAIR IN UG/L

A) DISTILLED WATER

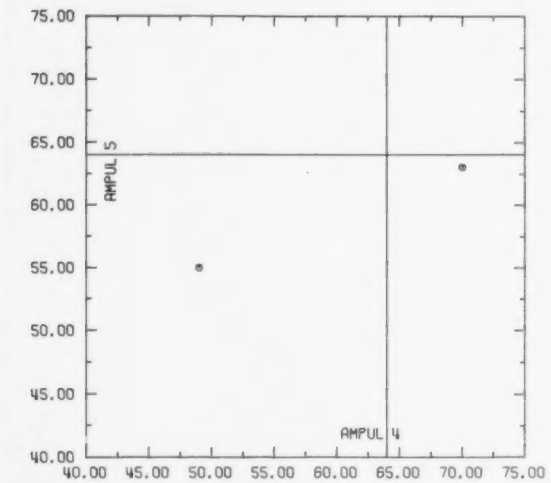


NATURAL WATER



MEDIUM CONCENTRATION PAIR IN UG/L

B) DISTILLED WATER



NATURAL WATER

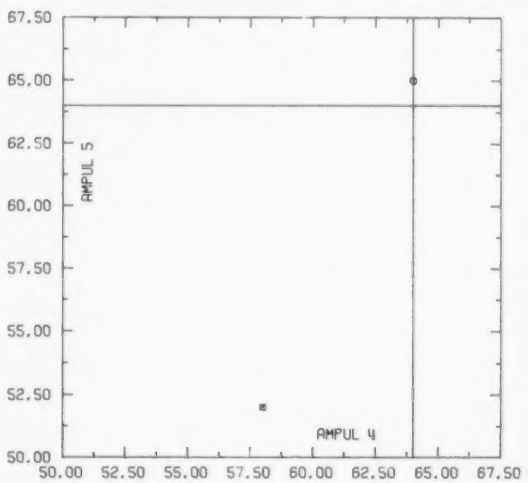
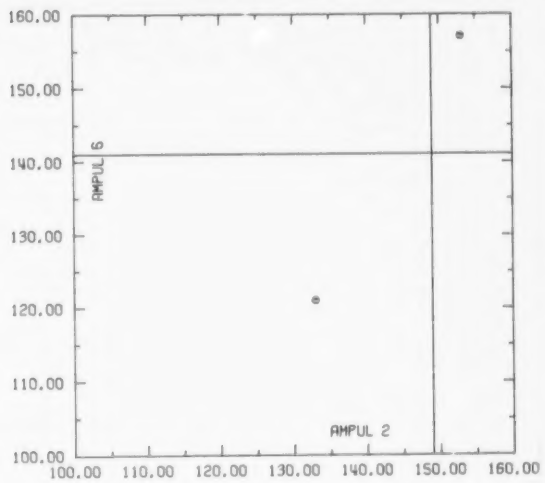


FIGURE 14
(continued)

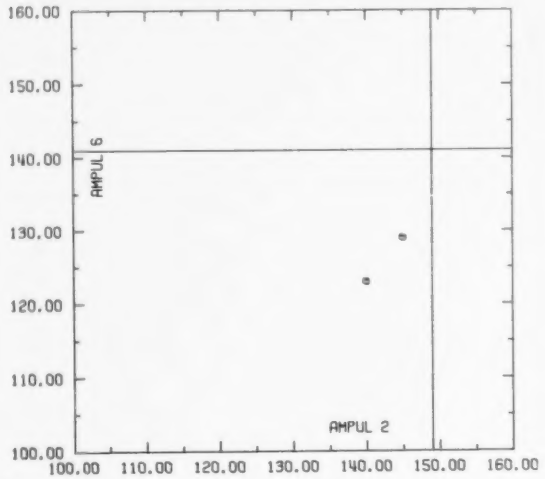
YOUDEN PLOTS FOR CYANIDE BY THE
ROBERTS-JACKSON METHOD

HIGH CONCENTRATION PAIR IN UG/L

C) DISTILLED WATER



NATURAL WATER



REFERENCES

1. Manual of Methods for Chemical Analysis of Water and Wastes. 1974. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

2. 1976 Annual Book of ASTM Standards. Part 31, Water. D2036-75.

3. Youden, W.J., 1967. Statistical Techniques for Collaborative Tests, Association of Official Analytical Chemists, Inc., Washington, D.C.

APPENDIX A

Instructions for EPA Method Study 12, Cyanide

U.S. ENVIRONMENTAL PROTECTION AGENCY
National Environmental Research Center

Instructions for EPA METHOD STUDY 12, CYANIDE

CAUTION: Read Instructions Carefully Before Opening Concentrates.

The requested set of sample concentrates are enclosed in this package. They were prepared by dissolving accurately weighed amounts of cyanide compounds in distilled water for exact and preplanned concentrations. When diluted according to instructions, the concentrations of cyanide will range from minimum detectable levels to those levels found in moderately polluted waters. Repeated analyses of the concentrates have verified that the solutions are stable and that the concentrations are correct.

There are six sample concentrates each to be diluted to volume with distilled water and if possible a treated waste effluent containing less than 0.05 mg/liter, total cyanide. If a waste effluent is not available, a river, lake, or salt water can be used. The waste effluent or natural water is analyzed with and without the spike and the spike's value determined by difference. The wastewater or natural water must not be chlorinated.

The prepared samples are to be analyzed for Total Cyanide and Cyanide Amenable to Chlorination using the methods cited in the manual: Methods for Chemical Analysis of Water and Wastes 1974, EPA. The necessary sections of this manual are enclosed. Since this study is intended to evaluate the precision and accuracy of the specified method, you are requested to use only the methods provided.

SAMPLE PREPARATION

When ready to begin, open the ampul by snapping the top off at the narrow point on the neck and dilute as follows:

Distilled Water Samples

Pipet 2 mL of 10 N NaOH and 5.0 mL of sample concentrate into a 1000 mL volumetric flask and make up to the volume with distilled water.

Wastewater/Natural Water Samples

If the wastewater/natural water sample was made alkaline with 2 mL of 10 N NaOH per liter at the time of collection, no hydroxide need be added. For the wastewater/natural water sample, pipet 2 mL of 10 N NaOH, if needed, into a 1000 mL volumetric flask, make up to volume with the wastewater/ natural water. For a spiked wastewater/natural water sample, pipet 2 mL of 10 N NaOH, if needed, and pipet 5.0 mL of sample concentrate into a 1000 of volumetric flask and make up to volume with the water.

We request the use of the pyridine-barbituric acid reagent if possible. Otherwise, the pyridine-pyrazolone reagent may be used. A 1 cm cell is to be used to make spectrophotometric readings.

The cyanide electrode procedure is enclosed as an additional method for analyzing the cyanide distillate. It is directed to those laboratories who have CN electrodes in use. The data should be reported along with the colorimetric data on the appropriate data sheet.

The analyses should be completed and data returned as requested to insure inclusion in the report. Return of data will be acknowledged promptly with a statement showing the true levels in the samples. If you have not already been assigned a laboratory code number, one will be assigned at that time. When all results have been received, the data will be evaluated statistically, and findings released to all participating laboratories in a formal EPA report.

If there are any questions or problems concerning the study, please contact:

Harold A. Clements
Quality Assurance & Laboratory Evaluation Branch
Methods Development & Quality Assurance Research Laboratory
National Environmental Research Center
Cincinnati, Ohio 45268

FTS: 513-684-2917

Encs: Report Forms
Parameter Values

Form Approved
O.M.B. No. 158-R 0025

Environmental Protection Agency
Quality Assurance & Laboratory Evaluation Branch
Methods Development & Quality Assurance Research Laboratory
Cincinnati, Ohio 45268

EPA METHOD STUDY 12, CYANIDE

DATA REPORT FORM 1

Colorimetric Procedure

Recovery of Cyanide, µg/liter

Distilled Water + 5 mL of Concentrate	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5	Conc 6
Total (CN)						
Amenable To Chlorination (CN)						
Waste Effluent or Natural Water + 5 mL of Concentrate	1	2	3	4	5	6
Total (CN)						
Amenable To Chlorination (CN)						
Waste Effluent or Natural Water	1	2	3	4	5	6
Total (CN)						
Amenable To Chlorination (CN)						

Please identify:

1) Spectrophotometer used _____ Cell Size _____

2) yridine-barbituric acid _____ Pyridine-pyrazolone _____

3) Identify Waste Effluent/Natural Water Used: _____

Comments _____

Analyst _____ Date _____

Laboratory _____ Lab. Code _____

Form Approved
O.M.B. No. 158-R 0025

Environmental Protection Agency
Quality Assurance & Laboratory Evaluation Branch
Methods Development & Quality Assurance Research Laboratory
Cincinnati, Ohio 45268

EPA METHOD STUDY 12, CYANIDE

DATA REPORT FORM 2

Electrode Procedure

Recovery of Cyanide, µg/liter

Distilled Water + 5 mL of Concentrate	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5	Conc 6
Total (CN)						
Amenable To Chlorination (CN)						

Waste Effluent or Natural Water + 5 mL of Concentrate	1	2	3	4	5	6
Total (CN)						
Amenable To Chlorination (CN)						

Waste Effluent or Natural Water	1	2	3	4	5	6
Total (CN)						
Amenable To Chlorination (CN)						

Identify Waste Effluent/Natural Water Used: _____

Comments _____

_____

Analyst _____ Date _____

Laboratory _____ Lab. Code _____

APPENDIX B

Analytical Methodology Used in EPA Method Study 12, Cyanide

1. Total Cyanide Pyridine-pyrazolone or Pyridine-barbituric Acid Methods

2. Total Cyanide - Electrode Method

3. Cyanides Amenable to Chlorination

5. Roberts-Jackson Method, Original Paper, Woods River Modification

CYANIDE, Total

STORET NO. 00720

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.2 mg/200 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentration below 1 mg/L of cyanide and is sensitive to about 0.02 mg/l.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurements uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver senstive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of cuprous ion.

4. Sample Handling and Preservation

4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly rinsed to remove soluble material from containers.

4.2 Samples must be preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.

4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

4.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure (8.1 through 8.5).

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the sample on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the stabilized sample (pH $\geq$ 12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with isooctane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be Fisher-Milligan scrubber.

6.2 Microburet, 5.0 mL (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

7. Reagents

7.1 Sodium hydroxide solution: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: powdered.

7.3 Ascorbic acid: crystals.

7.4 Cuprous Chloride Reagent: Weigh 20 g of finely powdered Cu_2Cl_2 into an 800 mL beaker. Wash twice, by decantation, with 250 mL portions of dilute sulfuric acid (H_2SO_4, 1+49) and then twice with water. Add about 250 mL of water and then hydrochloric acid (HCl, sp gr 1.19) in 1/2 mL portions until the salt dissolves (See Note 1). Dilute to 1 liter with distilled water and store in a tightly stoppered bottle containing a few lengths of pure copper wire or rod extending from the bottom to the mouth of the bottle (See Note 2).

NOTE 1: The reagent should be clear; dark discoloration indicates the presence of cupric salts.

NOTE 2: If it is desired to use a reagent bottle of smaller volume, it should be kept completely filled and tightly stoppered. Refill it from the stock solution after each use.

7.5 Sulfuric acid: concentrated.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 10.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 10 µg).

7.9 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 1.0 µg CN (1.0 mg/L).

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color Reagent - One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g or 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1,1'-diphenyl- 4,4'-bi-2 pyrazoline -5,5'dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide within 24 hours of preparation.

8. Procedure

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1 liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusing the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 25 mL conc. sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 10 mL of Cu_2Cl_2 reagent (7.4) into the air inlet and wash down with a stream of water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.5 Drain the solution from the absorber into a volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.6 Withdraw 50 mL of the solution from the volumetric flask and transfer to a 100 mL volumetric flask. Add 15 mL of sodium phosphate solution (7.6) and 2.0 mL of Chloramine T solution (7.12) and mix. Immediately add 5.0 mL pyridine-barbituric acid solution (7.13.1), or pyridine-pyrazolone solution (7.13.2.3), mix and bring to mark with distilled water and mix again.

8.7 For pyridine-pyrazolone solution allow 40 minutes for color development then read absorbance at 620 nm in a 1 cm cell. When using pyridine-barbituric acid, allow 8 minutes for color development then read absorbance at 578 nm in a 1.0 cm cell within 15 minutes.

8.8 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 mL with distilled water as follows:

mL of Standard Solution (1.0 = 1 µg CN)	Conc., When Diluted to 500 mL, mg/L CN
0(Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

8.8.1 Standards must be treated in the same manner as the samples, as outlined in 8.1 through 8.7 above.

8.8.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.3 Subsequently, at least two standards, one high and one low, should be treated as in 8.8.1 to verify standard curve. If results are not comparable (±20%), a complete new standard curve must be prepared.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to insure a level of 20 µg/L or a significant increase in absorbance value. Proceed with the analysis as in Procedure 8.8.1 using the same flask and system from which the previous sample was just distilled.

8.9 Alternatively, if the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.11 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

9. Calculation

9.1 Using the colorimetric procedure, calculate concentration of CN, mg/L, directly from prepared standard curve compensating for sample dilution if less than 500 mL was used for distillation.

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/L} = \frac{(A - B)\ 1000}{\text{mL original sample}} \times \frac{250}{\text{mL of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/L CN, the standard deviations were ±0.005, ±0.007, ±0.031, and ±0.094, respectively.

10.2 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN, recoveries were 85% and 102%, respectively.

BIBLIOGRAPHY

Bark, L. S. and Higson, H. G. "Investigation of Reagents for the Colorimetric Determination of Small Amounts of Cyanide." Talanta, 2:471-479 (1964).

Elly, C. T. "Recovery of Cyanides by Modified Serfass Distillation." Journal Water Pollution Control Federation, 40:848-856 (1968).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 498, Method D2036-72 Referee Method A (1973).

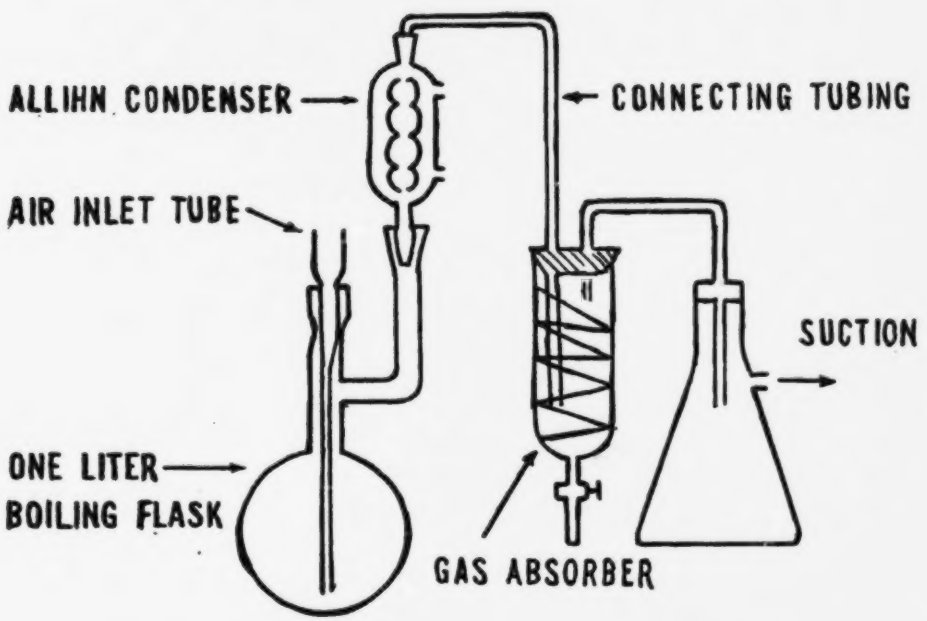


FIGURE 1

CYANIDE DISTILLATION APPARATUS

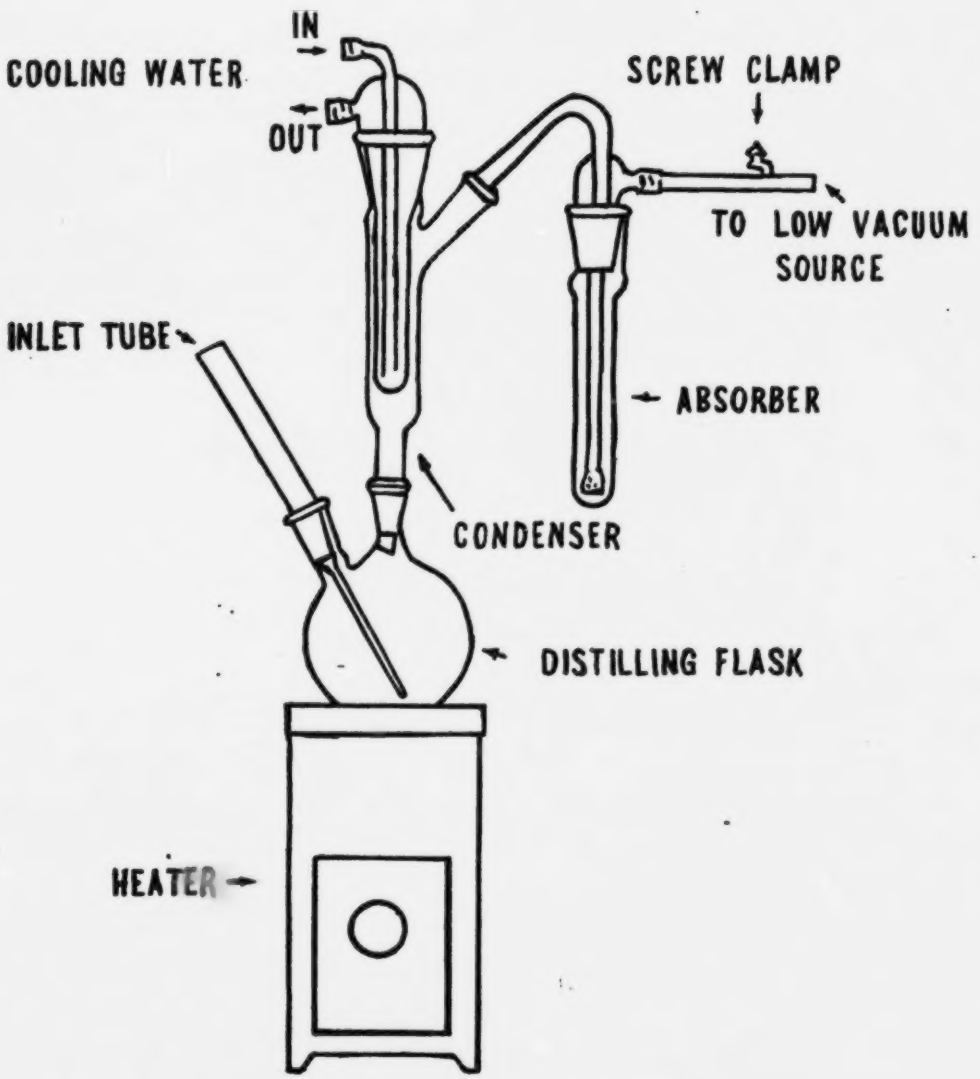


FIGURE 2

CYANIDE DISTILLATION APPARATUS

CYANIDE, TOTAL

(Electrode Procedure)

1. Scope and Application

   1.1 This procedure for determining total cyanide must be used on the scrubber solution obtained from the reflux-distillation operation as outlined in the method Cyanide, Total.

   1.2 All discussions under Sections 1-5 of the method Cyanide, Total, must be considered for application to this procedure.

2. Apparatus

   2.1 Electrometer (pH meter), with expanded MV scale, or a selective ion meter such as the Orion 400 Series.

   2.2 Cyanide Ion Activity Electrode, such as Orion No. 94-06.

   2.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

   2.4 Magnetic Mixer, Teflon-coated stirring bar.

3. Calibration

   3.1 Using a stock cyanide solution, prepare a series of standards in the concentration range expected in the reflux-distillation scrubber solution.

   3.2 The concentration of sodium hydroxide in the final cyanide standards and the reflux-distillation scrubber solution must be the same.

   3.3 Calibration of Electrometer: Proceed as described in Section 4 of this procedure.

      3.3.1 Using semilogarithmic graph paper, plot the concentration of cyanide in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

4. Procedure

4.1 Place a volume of scrubber solution or standard cyanide solution in a beaker and place on a magnetic mixer. The volume used must be consistent with the size of the electrode system and with the total scrubber solution volume.

4.2 Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution until the reading has stabilized. At low concentrations of cyanide, it may require as long as five minutes to reach a stable meter reading; higher concentrations stabilize more quickly.

NOTE: With some magnetic mixers it may be necessary to thermally insulate the sample from the mixer unit to eliminate any temperature change in the sample.

4.3 If a pH meter is used, record the potential measurement for each unknown sample. If a selective ion meter is used, read the cyanide level in the unknown sample scrubber solution directly in mg/L on the cyanide scale.

5. Calculation

5.1 Determine the concentration of cyanide in the scrubber solution from the calibration curve constructed in Section 3.3.1 or directly from the cyanide scale of a selective ion meter.

5.2 Calculate the concentration of cyanide in the original sample as follows:

$$CN, mg/L = A \times \frac{B}{C}$$

A = CN, mg/L in the scrubber solution from 5.1
B = Total scrubber solution volume in mLs
C = Total sample volume (in mLs) used in the reflux-redistillation

CYANIDES, Amenable to Chlorination

Storet No. 00722

1. Scope and Application

   1.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface, and saline waters, and domestic and industrial wastes.

   1.2 The titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/L after removal of the cyanides amenable to chlorination. Below this level the colorimetric determination is used.

2. Summary of Method

   2.1 A portion of the sample is chlorinated at a pH>11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Cyanide, Total, in this manual. Cyanides amenable to chlorination are then calculated by difference.

3. Reagents

   3.1 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 mL of distilled water.

   3.2 Sodium Hydroxide solution: Dissolve 50 g of sodium hydroxide ($NaOH$) in distilled water and dilute to 1 liter.

   3.3 Ascorbic acid crystals

   3.4 Potassium Iodide - starch test paper.

4. Procedure

   4.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 mL aliquot or a volume diluted to 500 mL, add calcium hypochlorite solution (3.1) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (3.2).

   Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

4.2 Test for residual chlorine with KI-starch paper (3.4) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

4.3 After one hour, add 0.5 g portions of ascorbic acid (3.3) until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.

4.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots as in the method Cyanide, Total, in this manual.

5. Calculation

5.1 Calculate the cyanide amenable to chlorination as follows:

CN, mg/L = A-B

where:

A = mg/L total cyanide in unchlorinated aliquot
B = mg/L total cyanide in chlorinated aliquot

BIBLIOGRAPHY

Annual Book of ASTM Standards, p. 503, Method B, 11.02, Water (11), p. 113. D2036-82, Method B-Cyanide Amenable to Chlorination by Difference (1983).

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Analyst, March, 1971, Vol. 96, *pp.* 209–212

The Determination of Small Amounts of Cyanide in the Presence of Ferrocyanide by Distillation under Reduced Pressure

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In the analysis of effluents and waters, the customary use of lead acetate to prevent the decomposition of ferrocyanide during the distillation of cyanide is not sufficiently effective when small concentrations of cyanide (about 0·1 mg l^{-1}) are to be determined. A method is described in which the decomposition of ferrocyanide can be completely prevented by distilling off the cyanide under reduced pressure in the presence of zinc acetate. The cyanide in the distillate is determined by the pyridine - pyrazolone method.

As very small amounts of cyanide can be toxic to fish, the method for the determination of cyanide in concentrations down to about 0·1 mg l^{-1} in water and effluent samples should be as precise as possible and free from interference from other constituents. The usual procedure is to distil a large amount of an acidified sample, absorb the evolved hydrogen cyanide in a small amount of sodium hydroxide solution and finally determine the cyanide content spectrophotometrically. If the sample contains ferrocyanide, which is relatively non-toxic, the latter would partially decompose during distillation and release hydrogen cyanide, thus giving rise to positive errors. The use of lead acetate to prevent the decomposition of ferrocyanide is included in certain recommended methods of analysis of sewage and trade effluents.[1,2] These methods, however, refer to the determination of relatively large concentrations of cyanide (about 10 mg l^{-1}). Other work[3,4] in which lead acetate was used for this purpose involved milligram amounts of cyanide, which could be determined titrimetrically. Our experience has shown that lead acetate does not completely prevent decomposition of ferrocyanide and is inadequate when small amounts of cyanide are involved.

Experimental

Several synthetic samples were prepared containing small amounts of potassium cyanide and ferrocyanide. Distillations were carried out on these samples, after adding lead acetate to the distillation flask, and the absorbed hydrogen cyanide was determined spectrophotometrically by using a slightly modified form of the pyridine - pyrazolone method.[5] High results were obtained for each sample. Further tests were then carried out in which the lead acetate was replaced by zinc acetate, the use of which has also been recommended[6] as a way of preventing the decomposition of ferrocyanide, and although zinc acetate was much more effective than lead acetate, it did not completely prevent the breakdown. Typical results obtained with lead and zinc acetates are given in Table I.

Table I

Known amounts of cyanide and ferrocyanide distilled in the presence of lead acetate and zinc acetate

Test No.	Distillation conditions	Ferrocyanide added/ mg l^{-1} of $K_4Fe(CN)_6$	Cyanide added/ mg l^{-1} of CN	Cyanide found/ mg l^{-1} of CN
1	With lead acetate	0	0·033	0·034
2		0·033	0·033	0·045
3		6·66	0·033	1·27
4		20·00	0	7·6
5	With zinc acetate	13·3	0	0·05
6		20·0	0·125	0·04

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Various modifications were made to the procedure and finally it was found that the decomposition of ferrocyanide could be prevented by carrying out the distillation at a controlled reduced pressure in the presence of zinc acetate. Several synthetic samples were then examined by this method and good recoveries of small amounts of cyanide were obtained, even in the presence of relatively large amounts of ferrocyanide. Typical results are given in Table II. The procedure used does not prevent the decomposition of all other cyanide complexes but in some instances, *e.g.*, tripotassium pentacyanocarbonylferrate $\{K_3[Fe(CN)_5CO]\}$ and disodium pentacyanonitrosylferrate $\{Na_2[Fe(CN)_5NO]\}$, the amount decomposed is reduced.

The method has been used effectively on samples of effluents and waters during the last few years.

TABLE II

KNOWN AMOUNTS OF CYANIDE AND FERROCYANIDE DISTILLED AT REDUCED PRESSURE IN THE PRESENCE OF ZINC ACETATE

Test No.	Sample	Ferrocyanide added/ mg l^{-1} of $K_4Fe(CN)_6$	Cyanide added/ mg l^{-1} of CN	Cyanide found/ mg l^{-1} of CN
1	Distilled water	0·033	0·033	0·033
2		0·66	0·033	0·033
3		0·66	0·042	0·043
4		13·3	0	0·002
5		13·3	0·033	0·034
6		13·3	0·083	0·082
7		13·3	0·167	0·168
8		13·3	0·334	0·334
9		20·0	0·125	0·123
10		20·0	0·500	0·500
11	River water	0	0	0·004
12		1·0	0·056	0·056
13		1·0	0·054	0·055
14	Effluent containing	0	0	0·003
15	$CaCl_2$ and NaCl	1·0	0	0·002
16		1·0	0·062	0·060
17		1·0	0·062	0·063

Tests 5 to 10 were repeated on samples containing 10 per cent. w/v sodium chloride solution and similar results were obtained.

METHOD

APPARATUS—

An all-glass distillation apparatus is set up as shown in Fig. 1. The components are obtainable from laboratory suppliers, with the exception of the 250-ml absorption flask, which has been modified by means of a thimble-type extension, of about 10-ml volume, to the base of the flask. The delivery tube passes to the bottom of the thimble. This modification ensures that hydrogen cyanide evolved in the early part of the distillation passes into an an adequate column of absorption solution.

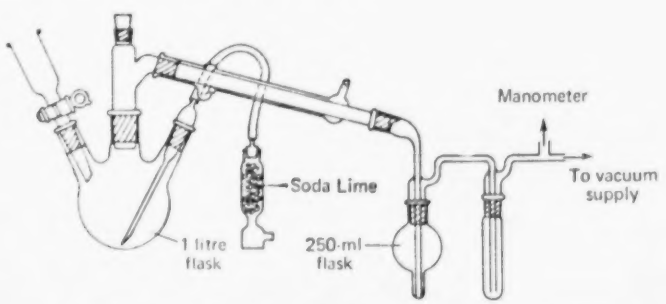

Fig. 1. Apparatus for distillation of cyanide under reduced pressure

REAGENTS—

Sodium hydroxide, 0·1 N.

Hydrochloric acid, 0·1 N.

Zinc acetate solution, 10 *per cent. w/v.*

Phenolphthalein indicator solution, 0·1 *per cent. in ethanol - water* (1 + 1).

Acetic acid solution, 0·5 *per cent. v/v.*

Chloramine T solution, 1·0 *per cent. w/v in distilled water*—This solution should be prepared daily.

3-*Methyl*-1-*phenyl*-5-*pyrazolone solution*—Dissolve 2·5 g in 500 ml of distilled water and warm the solution to 70 °C, while stirring. Allow the solution to cool in the dark, and store in a dark bottle; filter before use. Renew the solution after 5 days.

Bispyrazolone [3,3'-*dimethyl*-1,1'-*diphenyl*-(4,4'-*bi*-2-*pyrazoline*)-5,5'-*dione*] *solution*—Add 0·025 g to 25 ml of analytical-reagent grade pyridine and allow the mixture to stand in the dark, occasionally shaking it until the reagent is dissolved (about 1 hour).

Mixed pyridine - pyrazolone reagent—Filter 125 ml of 3-methyl-1-phenyl-5-pyrazolone solution into a brown bottle, add bispyrazolone solution and store in the dark. Prepare daily.

Stock standard cyanide solution—Dissolve 0·251 g of analytical-reagent grade potassium cyanide in 1 litre of distilled water containing 20 ml of 0·1 N sodium hydroxide.

Dilute standard cyanide solution—Dilute 10 ml of the stock solution to 1 litre with distilled water. This solution should be freshly prepared.

1 ml of solution contains 1·0 μg of cyanide.

PREPARATION OF CALIBRATION GRAPH—

Into a series of 50-ml standard flasks, introduce accurately measured volumes of the dilute standard cyanide solution containing 0, 2, 4, 6, 8 and 10 μg of cyanide and dilute to about 20 ml with distilled water. Add 2 drops of phenolphthalein solution, neutralise with acetic acid solution and add 0·1 ml in excess. Add 0·2 ml of chloramine T solution and allow to stand for 1½ minutes. Then add 15 ml of mixed pyridine - pyrazolone solution, mix and allow the mixture to stand for 30 minutes in the dark. Make up to 50 ml with distilled water and measure the optical density of the solution in a spectrophotometer at a wavelength of 620 nm with a 10-mm cell, with distilled water in the comparison cell.

Correct the readings for the reagent blank and plot a calibration graph relating net optical density to cyanide content.

METHOD OF CARRYING OUT THE TEST—

Introduce into the distillation flask a volume of up to 600 ml of a sample of the water or effluent, and connect the apparatus shown in Fig. 1, with the absorption flask containing 10 ml of 0·1 N sodium hydroxide and guard tube 5 ml of 0·1 N sodium hydroxide.

Titrate a separate portion of the bulk sample with 0·1 N hydrochloric acid to determine the amount of acid required to neutralise the volume of sample in the distillation flask. Add this amount of 0·1 N hydrochloric acid to the distillation flask followed by an additional 10 ml. Then add 10 ml of 10 per cent. zinc acetate solution. Connect the air inlet tube to the soda lime column and evacuate the apparatus to reduce the pressure inside to between 127 and 254 mm of mercury, while maintaining slow bubbling from the capillary of the air inlet tube. Heat the flask and boil the solution steadily until a total volume of about 75 ml is collected in the absorption flask. Stop the distillation by removing the source of heat, turn off the vacuum and allow the pressure to return to atmospheric by continuing the bubbling.

Combine the absorption and guard tube solutions and make up to volume in a 100-ml standard flask. Measure a suitable aliquot from the 100-ml standard flask (usually 20 ml) into a 50-ml standard flask and proceed with the colour development and optical density measurement as described under "Preparation of Calibration Graph."

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WOODS RIVER MODIFICATION OF ROBERTS METHOD FOR SIMPLE CYANIDE

A. Distillation

1. Measure 500 mL of sample.

2. Measure a separate 50 mL of sample, add 5 drops of phenolphthalein, and then titrate with 1N HCl to the phenolphthalein end point. Note the volume of 1N HCl required for titration. This volume is multiplied by ten, plus one additional mL, to determine the volume to be added to the 500 mL sample prior to distillation (see No. 4. below).

3. Assemble the distillation apparatus as specified in the EPA Method for total cyanide, and add 50 mL of 1N NaOH to the absorber. Add the 500 mL of sample to the distillation flask and place the air delivery tube in position. Adjust the air flow for a low, smooth flow. (.500 mL/min)

4. Add the required volume of 1N HCl, as determined in No. 2 above, through the air delivery tube and rinse with a small amount of distilled water. Then add 10 cc of 10% Zinc Acetate solution through the delivery tube and rinse.

5. Adjust the heater to a previously determined setting which will maintain a vigorous boiling rate with refluxing approximately 1/3 to 1/2 the condenser length. Caution the air flow must be watched very closely at the time when boiling begins to prevent the contents of the flask from backing out of the delivery tube.

6. After boiling begins, allow one hour refluxing. Then remove heat and allow the flask to cool for an additional 15 minutes. Remove the absorber and transfer the contents to a 250 mL volumetric flask. Rinse the absorber several times to insure quantitative transfer of the distillate. Dilute to volume with distilled water.

B. Color Development

1. Transfer 50 mL of the distillate to a clean 100 mL volumetric flask.

2. Prepare a 0.100 ppm standard by first adding exactly 49 mL of 0.2 N NaOH to a clean 100 mL volume flask and then add one (1) mL of the intermediate cyanide standard (do not add H_2O).

3. Add 20 mL sodium dihyrogen-phosphate solution to each of the 100 mL flasks containing the sample distillates and the 0.100 ppm standard. Swirl and mix the reagent.

4. Add 2 mL of Chloramine T solution to the first flask, note the time, invert the flask three (3) times and then swirl to mix. Wait one (1) minute and then add 5 mL of the Pyridine-Barbituric Acid solution and immediately swirl and mix.

5. Fill to mark with distilled water and mix thoroughly. Repeat in succession for the second and third.

6. Allow 10-15 minutes after the addition of the Chloramine T Solution for color development and then read the absorbance at 578 nm using a 2 cm cell.

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References

1. Ministry of Housing and Local Government, "Methods of Chemical Analysis as applied to Sewage and Sewage Effluents," H.M. Stationery Office, London, 1956.
2. The Association of British Chemical Manufacturers and the Society for Analytical Chemistry, "Recommended Methods for the Analysis of Trade Effluents," W. Heffer & Sons Ltd., Cambridge, 1958.
3. Jenkins, S. H., Hey, A. E., and Cooper, J. S., *Air Wat. Pollut.*, 1966, **10**, 495.
4. Feld, W., *J. Soc. Chem. Ind., Lond.*, 1903, **22**, 1068.
5. American Public Health Association (American Water Works Association and Water Pollution Control Federation "Standard Methods for the Examination of Water and Wastewater," Eleventh Edition. APHA Inc. 1790, Broadway, New York 19, N.Y., 1960.
6. Russell, F. R., and Wilkinson, N. T., *Analyst*, 1959, **84**, 751.

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